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INVESTIGATION OF REACTIVITY OF LAUNCH VEHICLE MATERIALS WITH LIQUID OXYGEN

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INVESTIGATION OF REACTIVITY OF LAUNCH VEHICLE MATERIALS WITH LIQUID OXYGEN

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ABSTRACT

This is the final report for a study of the impact sensitivity of organic compounds in liquid oxygen. The principal objectives of this work were to elucidate the mechanism of impact ignition in LOX and to establish the relationship between sensitivity and chemical and physical properties.

The program consisted of two phases. The first phase was concerned with measurements of impact sensitivity using a modified ABMA drop-weight tester. For eighteen of the twenty four compounds tested, a positive correlation was found between the relative sensitivity and flash point. Five other compounds, in two groups, displayed a correlation between sensitivity and chemical reactivity in autoxidation. Similar correlation were observed for these same compounds in hot-wire ignition tests. A few experiments designed to clarify the mechanical factors affecting impact sensitivity showed that misalignment of the striker pin was of major importance. Dibromomethane added to benzene and cumene markedly reduced their sensitivity. Still and high-speed photography of the impact ignition of benzyl alcohol provided evidence for a point source (hot spot) ignition mechanism.

The second phase was concerned with the relative reactivity of t-butoxy and t-butyl peroxy radicals towards a variety of organic compounds at 50 and 100°. A good correlation as found between relative reactivity of both radicals toward five hydrocarbons. However the correlation for four aliphatic derivatives was less good suggesting that differing electronic requirements for these compounds is the major factor governing reactivity. There is no correlation between reactivity in oxidation and impact sensitivity for the aliphatic compounds tested. The oxidation of hexamethyl dialuminum occurs spontaneously and rapidly at -140° by a mechanism involving displacement of oxygen on the bridge-head Me-Al bond followed by rearrangement of the initial MeOO-Al complex at -80° to give the stable MeO-Al structure.

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I INTRODUCTION

Many materials in contact with liquid oxygen (LOX) are explosion hazards when subjected to impact, heat, or other forms of energy. The selection of materials for safe use in a LOX environment is based on an arbitrary test that subjects such materials to impact under LOX. Rocket construction materials selected by this empirical method have been satisfactory, but it is possible that some materials that could be adequate have been eliminated. Improved selection methods are needed, but design of such methods is dependent upon a more complete knowledge of the conditions and mechanisms necessary for ignition in the presence of LOX. The objective of this study is to examine and identify these conditions and mechanisms.

Explosions or rapid oxidations, resulting from impacting organic compounds in the presence of LOX very likely involve formation of carbon radicals at elevated temperatures following conversion of mechanical to heat energy. Neither the way in which these radicals are initially produced nor the way in which they are converted to final products in exothermic reactions with oxygen is well understood. Such knowledge seems essential for predicting or altering the behavior of impact-sensitive systems.

Oxidation of organic compounds at elevated temperatures is usually a complicated free radical chain reaction involving initiation from some free radical source, propagation, and termination. The important features of these reactions are well known for hydrocarbons but much less clear for their derivatives. Because of the important role of free radicals in ignition processes at elevated temperatures, some measure of the relative reactivity of organic compounds toward such radicals seems important in understanding the observed range of sensitivities in impact ignition.

This is the final report for the NASA-supported study of the mechanism of impact sensitivity for organic compounds in liquid oxygen under Contract No. NAS8-21316 and the third annual report on this

program, previously supported under Contract NAS8-20220. Earlier work[1] showed that although free radicals may be generated either mechanically or photochemically at low temperatures, no chain reactions occur and the intermediate polyoxides that are formed decompose slowly to stable products above -30°. The evidence strongly favors some mechanism by which the mechanical energy of the impact is converted into heat energy at discrete sites. This so called "hot spot mechanism" requires that the actual combustion process occur at elevated temperatures following volatilization of the substrate.

The present program is divided into two parts, one of which is concerned with those factors involved in impact sensitivity, including drop-weight testing, thermal ignition by other sources, and high speed photography of the impact ignition phenomena. The second part is concerned with the chemical factors affecting sensitivity, such as relative reactivity of organic compounds to radicals involved in combustion processes and the special cases of spontaneous low temperature ignition of alkyl aluminum compounds.

The results of both phases should permit a better correlation of the physical and chemical properties with ignition and thus permit improved design and/or selection of safer materials.

II IMPACT STUDIES

A. Background and Theory

The reactivity of an organic material with liquid oxygen is judged by its impact sensitivity as measured with the A.B.M.A. drop-weight tester, or a similarly designed tester. Many materials--greases, lubricants, gaskets, sealants--have been evaluated (that is, accepted or rejected) for their potential use in liquid oxygen with this technique. Yet little is known about the impact-initiated mechanisms involved in the reactions of LOX and organic materials. Bowden[2] has determined that liquid and solid explosives, when impacted, are initiated by hot spots. These hot spots, of some small volume, occur at the sites of small entrapped bubbles of gas or high-melting extraneous grit particles. It is not certain that this so-called hot-spot theory applies to materials in a LOX environment but it was adopted as a working basis for our experimental program during the preceding year.

Assuming the applicability of the hot-spot theory, the mechanisms for ignition by mechanical impact must be basically similar to thermal mechanisms that operate in more conventional circumstances: The impact-produced hot spot causes pyrolysis and vaporization of organic material; some minimum concentration of flammable vapor must be produced and diluted with oxygen to form a flammable mixture; finally, the mixture must be heated to the ignition temperature.

If the hot-spot theory is valid the impact sensitivity of any flammable material should be determined by the same factors that determine the sensitivity of that material to ignition and sustained combustion under conventional circumstances. These factors are molecular weight, chemical structure and reactivity, vapor pressure, flash point, auto-ignition temperature, etc.

Therefore, it is reasonable to expect that the order of sensitivity in a given series of organic compounds as determined by the impact apparatus should be in reasonable agreement with the order as determined by another method. During this past year results obtained with thermal

ignition apparatus (hot spots generated with a hot wire) have been compared with impact sensitivity data. The thermal ignition method was adopted since it provided more information regarding the variables that are pertinent to the impact process, i.e. ignition temperature and ignition delay time.

Evidence as to whether hot spots are involved in the ignition process may be obtained photographically. Still and high-speed photography have provided information as to the actual initiation and propagation phenomenon occurring upon impact of a sample of benzyl alcohol, a very LOX impact-sensitive organic compound.

B. Summary

A selected group of organic compounds have been impact tested with the ABMA drop-weight tester. Attempts have been made to correlate the impact sensitivities of these compounds with their physical properties and chemical structure. In some instances subgroups of compounds that are structurally similar have exhibited sensitivities correlating with their flash points, i.e., the compounds with the lowest flash points have been found to possess the highest impact sensitivity. Chemical structure has been shown to be a factor in impact sensitivities of cumene, toluene, and t-butylbenzene.

The impact and rebound sensitivities of materials has been shown to be somewhat variable depending on the testing technique used. One of the major causes of this variability is thought to be the misalignment of the striker pin.

The addition of small percentages of fire-retardants to two very impact sensitive compounds, benzene and cumene has dramatically reduced their sensitivities. The effects of retardants on the impact sensitivities of a few polymers have also been investigated.

A few of the compounds that were impact tested were ignited by the hot-wire method, and minimum ignition temperatures and ignition-delay times were measured. The hot-wire sensitivity of compounds within certain sub-groups were again found to correlate with physical property variations and furthermore, hot-wire data appear to agree with impact data.

Still and high-speed photography have been utilized to determine the actual ignition and propagation mechanism occurring in a material when it is impacted in a LOX environment.

Two preliminary experiments leading to the use of high-speed photography for the study of impact-induced ignition mechanisms were performed. In one of these the amount of light from the reaction flash was observed and the sample ignition area estimated from photographs taken with a still camera. In the other experiment the light intensity of the flash was measured and two important times determined: (1) the delay time from impact of plummet and striker pin to ignition and (2) the duration of the flash. High-speed photography of the impact of benzyl alcohol at framing rates of 14,000 pictures per second has shown that ignition initiates from a point source in the compressed area of the sample below the striker pin face.

C. Impact Studies

It was hypothesized that an organic material exhibits a certain LOX reactivity or impact sensitivity dependent (partially at least) on its physical properties and chemical structure. To test this hypothesis impact tests were performed on a selected series of pure organic compounds for which physical property data was readily available. These impact tests were performed on the A.B.M.A. apparatus at drop heights of 43 inches by two different techniques: (1) using the standard striker-pin guide, and (2) using retainer springs on top of the striker-pin guide to hold striker-pins firmly in alignment.

1. Physical-Chemical Property Correlations

The physical properties felt to be pertinent to the impact studies were melting and boiling points, flashpoint, autoignition point, heat capacity, and latent heats of fusion and vaporization. The value, ΔH_T, the sum of the heat capacity, heat of fusion and heat of vaporization was tabulated for convenience. Chemical structural properties thought to be important to the impact studies were those that would effect the ease of oxidation of the organic compound.

The impact sensitivities and pertinent physical properties of the compounds that have been examined are shown in Table I. These compounds, by nature of their chemical structures, fall into various subgroups, which are discussed below.

Table I

IMPACT SENSITIVITY VERSUS PHYSICAL PROPERTIES FOR PURE ORGANIC COMPOUNDS[a]

Compounds	Impact Sensitivity						Physical Properties									ΔH_T[b]
	Ht. (in.)	Reactions / Trials	1st	2nd	3rd	Conditions	M.P. (°C)	B.P. (°C)	Flash Point (°C)	Auto Ignition Temp. (°C)	Cp Cal/gm @ °C		ΔH_f Cal/gm	ΔH_v Cal/gm @	ΔH_v Normal b.p. °C	
Benzene	24	6/10	4	2		W/O Retainer	+5.5	80.1	-11	580	0.4180 .379	27.5 0	30.25	94.16	80	125
	43	16/21	15	1		W Retainer					.154	-173				
	43	8/11	7	1		W/O Retainer										
Chlorobenzene	24	2/10	1	1	W/O	W/O Retainer	-55	132	32	693	.3191	26.8	20.29	77.4	130.6	97.7
	43	3/10	3			W Retainer					.2916	-43.2				
	43	4/10	2	2		W/O Retainer					0.1067	-183				
Bromobenzene	24	4/10		4		W/O Retainer	-30.6	156	65	688	.2368	26.8	16.18	57.6	155.9	73.8
	43	0/10				W Retainer					.1845	-33.2				
	43	3/10	1	2		W/O Retainer					.0836	-183				
O-dichlorobenzene	43	1/10	1			W Retainer	-17	179	151		0.27	0	21.7	64.5	179	86.2
	43	3/10		3		W/O Retainer										
P-dichlorobenzene	43	0/10				W Retainer	53	174	150		0.298	53	29.6	63.04	174	92.6
	43	3/10	2	1		W/O Retainer										
Naphthalene	24					W Retainer	80.2	218	79	567	.3088 .1009	21.5 -189	35.06	43.5	218	78.6
	43	0/10				W Retainer										
	43	2/10	2			W/O Retainer										
Anthracene	24	0/10				W Retainer	218	342	121	472 (O_2)	0.381	150	38.7	119	342	158
	43	0/10				W Retainer					0.308	50				
	43	0/10				W/O Retainer										
Hexane							-94	69	-22	248	.5447 ..3459	27.8 -99	36.3	87.5	25	124
	43	6/10	3	2	1	W Retainer					0.2024	-189				
	43	5/10	4	1		W/O Retainer										
Hexyl alcohol	43	0/10				W/ Retainer	-44.6	157	62.7		0.4956		35 (est)	98.5 (calc)	157	134
	43	6/10	3	3		W/O Retainer										
Hexanoic acid	43	0/10				W Retainer	-3.95	205	>80		0.533	29	30-35 (est)	98.5 (calc)	205	~130
	43	2/10	1	1		W/O Retainer										
Cyclohexane							6.5	80.7	-17	296	0.4411 0.1462	19.3 -190	7.569	94.82	25	102.4
	43	4/10		2	2	W Retainer										
	43	3/10		3		W/O Retainer										
Cis-decalin[c]	43	4/10	1	3		W Retainer	-43.2	195	58	262	0.396	20.55	16.4	73.5	194.5	89.9
Toluene	43	5/10	3	2		W Retainer	-94.99	110.6	4.3		0.421	50	17.17	86.80	110.6	103.97
	43	7/10	5	2		W/O Retainer										
Cumene	43	7/10	6	1		W Retainer	-96.03	152.4	38.8				14.15	74.60	152.42	88.75
	43	9/10	7	2		W/O Retainer										
Tert-Butylbenzene	43	1/10	1			W Retainer	-57.85	169.5	<7.6				14.93	68.61	169.5	83.53
	43	4/10	1	3		W/O Retainer										

[a] Cumulative table of data.
[b] Sum of ΔH_v, ΔH_f.

Table I (continued)

Compound	Impact Sensitivity Ht., in.	Reactions Trials	1st	2nd	3rd	Conditions	M.P. (°C)	B.P. (°C)	Flash Point (°C)	Auto Ignition Temp. (°C)	Cp Cal/gm	Cp @ °C	ΔH_J Cal/gm	ΔH_V Cal/gm	ΔH_V @ °C	ΔH_T
Isopropyl Alcohol	43	3/20		3		W. Retainers	-88.5	82.26	11.7-14.5	456	.0507	-200	21.0	160	82.3	181.58
	43	3/20		3		W/O Retainers					~.58	25				
Isopropyl Acetate	43	2/20		2		W. Retainers	-73	93	6	460	.46	25	~25(est.)	74.2	93	99 (est.)
	43	6/20		6		W/O Retainers										
Isopropyl Ether	43	6/20	2	4		W. Retainers	-85.89	69	-28	443	0.528	25	25.79	68.2	69	94.5
	43	10/20	3	7		W/O Retainers										
ter-Butyl Amine	43	2/14	1	1		W. Retainers	-67.5	45.2	-9		0.627	25	20(est.)	96.5	45.2	116 (est.)
	43	3/20		3		W/O Retainers										
Hydroquinone	43	8/10	8			W. Retainers	170 (172)'	285	165							
p-Dihydroxy-benzene	43	10/10				W/O Retainers					0.304	25	58.8			
Resorcinol	43	0/10				W. Retainers	111	281	127		0.284	25	46.2			
m-Dihydroxy-	43	0/0				W/O Retainers	(110)	(275.9)								
Hexane	43	6/10	3	2	1	W. Retainers	-94	69	-22	248	0.5447	27.8	36.3	87.5	25	124
	43	5/10	4	1	1	W/O Retainers										
Dodecane	43	2/10	1		1	W. Retainers	-9.58	216.3	165		0.521	24.54	51.69	86.0	25	
	43	2/10		2		W/O Retainers										
Polyethylene	43	0.20				W/O Retainers	137.5		340							

Benzene and its halogenated derivatives (chlorobenzene, bromobenzene, o-dichlorobenzene and p-dichlorobenzene) were impacted at 43 inches. Chemical structural variations within this subgroup would not be expected to have an appreciable effect on impact sensitivity. But consideration of the physical properties indicates a correlation between the impact sensitivities of these compounds and their flash points, i.e., the compounds with the lowest flash points possess the highest impact sensitivities This same result has been found with other subgroups.

With the aromatic series of benzene, naphthalene, and anthracene increasing molecular weight and flashpoints are accompanied by regularly decreasing impact sensitivity.

The impact sensitivities of hexane, hexyl alcohol and hexanoic acid are in the order of reactivity (hexane > hexyl alcohol > hexanoic acid) which again correlates inversely with the order of flash points. Of these three compounds, hexyl alcohol is most easily oxidized by other methods (see Sect. II). Therefore, the much lower flash point of hexane appears to be the important factor making it more impact sensitive than the alcohol. Hexanoic acid, with the highest flash point, is the least impact sensitive of this group. It is also the least susceptable to autoxidation by other methods.

In the hydrocarbon series hexane (flash point $-22^{\circ}C$), cyclohexane (flash point $-17^{\circ}C$), and cis-decalin (flash point $58^{\circ}C$), cis-decalin exhibits a much greater reactivity than might be predicted from flash point considerations. This higher sensitivity may be due to the presence of tertiary hydrogens at the bridge-head carbon atoms. Finally, the impact sensitivities of hexane, dodecane, and polyethylene, members of the straight chain hydrocarbon series, were found to correlate with their flash points. In this subgroup, this variation in sensitivity may also be explained as follows: the increasing molecular weight, melting points, and boiling points from hexane to polyethylene is accompanied by a corresponding decrease in vapor and by a decrease in susceptibility to ignition.

We may conclude from the results obtained in the previous subgroups that when compounds are very similar in chemical structure it is likely that their flash points can provide some information on their relative impact sensitivities.

The following subgroups of organic compounds show how the impact sensitivity can also depend on the chemical structure of the compound being evaluated. The impact sensitivity of the series t-butylbenzene, toluene, and cumene is given in Table I. The sensitivity of these compounds increases in the order t-butylbenzene < toluene < cumene--the same order of sensitivity as that found for reactivity toward peroxy radicals in the liquid phase oxidation of these compounds.[3] There is no obvious correlation with the flash points. We conclude that, in this series of substituted aromatics, free radical reactivity is a better criterion for impact sensitivity than flash point. This is probably the case because of the much greater range of free radical reactivity of these compounds as compared to the other benzene derivatives, all of which are relatively inert to oxidation under mild conditions. At 30°, the relative rates of attack by a peroxy radical on t-butylbenzene, toluene, and cumene (on a per hydrogen basis) are ~0.001, 0.03, and 0.5.[3]

Hydroquinone (1,4-dihydroxybenzene) and resorcinol (1,3-dihydroxybenzene) are two benzene derivatives that possess very similar physical properties. But the difference in their susceptibility towards oxidation is great: hydroquinone is easily oxidized with oxygen by a free radical mechanism, while resorcinol is oxidized with difficulty by this same method.[4] The impact sensitivities and physical properties of these two compounds are shown in Table I. Hydroquinone is very sensitive to LOX impact whereas resorcinol is very insensitive. This is a case where chemical reactivity clearly dominates the response of these two compounds, for the physical properties related to flammability indicate the meta isomer should be the more reactive. The melting point of the meta isomer is 60° lower than the para isomer, the boiling point is 4° lower, and the flash point of $127^{\circ}C$ is 38° lower than the flash point, $165^{\circ}C$, of p-dihydroxybenzene.

Both of these subgroups exhibit differences in reactivity (impact sensitivity) that are apparently caused by variations in chemical rather than in physical properties. When these compounds are oxidized under standard conditions the compounds exhibit an oxidation reactivity dependent upon their free radical reactivity. Since the impact sensitivities of the compounds within these two subgroups correlate with their known free radical reactivities, it may be surmised that the free radical mechanism may be operative in a reaction occurring in a LOX environment.

2. Effect of Varying Test Method

Initial studies of impact sensitivity revealed the striker pin was severely displaced in the period between initial and first rebound impact of the falling weight. This was corrected by holding the guide plate firmly against the flange on the striker pin, with a spring on each of the three guide bolts. This restriction on the striker pin resulted in noticeable changes in initial impact and rebound ignition frequencies for compounds previously tested. The variables causing these changes were of interest since they may be responsible for deviations in impact test results emanating from different laboratories. All subsequent tests were therefore run both with and without the use of the retainer springs.

The importance of this variation in test method is verified when all the data presented in Table I is considered. The significance of the observation relative to ignition mechanisms is not clear. Naphthalene gave no reactions when spring retainers were used, but gave two reactions when retainers were eliminated. However, observations on the unreacted samples help to explain these results. When spring retainers were used on the striker pin guide, the samples were only slightly chipped by the impact, but when spring retainers were not used, the brittle polycrystalline samples of naphthalene and anthracene were shattered. Some pieces were even thrown from the sample cup. It is possible that a shattered sample produced on impact reacts more readily than a sample that remains intact.

The isopropyl compounds are interesting examples of how impact sensitivity and rebound ignition frequency change with changes in the test method. When retainer springs were not used with isopropyl ether, one more initial and three more rebound reactions occurred. Four more rebound reactions were obtained with the acetate when retainer springs were left off.

Toluene and cumene both gave two more positive impacts out of 10 tests when retainer springs were not used. Bromobenzene was insensitive when retainer springs were applied, but reacted three out of 10 trials when the springs were removed.

From this evidence it is clear that compounds are generally more sensitive to both initial and rebound impact when retainer springs are not used. Three variables appeared to be operating to make a sample more impact-sensitive when the retainer springs were not used: (1) mechanical shear imparted to the sample by misalignment of the striker pin (non-coplanarity of anvil and striker-pin faces) initially, or on rebound, (2) higher stress concentration also caused by misalignment of striker pin, and (3) the creation of much new surface by the initial impact, and the subsequent reaction of the "new" sample on rebound.

The first variable would certainly produce in the sample a region of high stress concentration where the probability of a hot-spot would be greater than if the pin and anvil faces were parallel. The second variable would increase the probability of ignition by providing crystals that individually would be much simpler to ignite because of a sample of higher surface-to-weight ratio that would enhance energy transfer. These variables represent serious and uncontrolled parameters in the mechanics of the impact apparatus.

3. Fire Retardants

The addition of small percentages of fire-retardants to materials often reduces their flammability. Since the impact sensitivity of a material in LOX is related to its flammability, it seemed reasonable that the impact sensitivity of a material could be reduced by a retardant.

This hypothesis was tested in a few preliminary experiments with a phenolic and a vinyl chloride polymer, plus benzene and cumene, two very impact-sensitive compounds.

Dibromomethane, a flame inhibitor, was added to benzene and cumene and the mixtures impacted at 43 inch heights with the ABMA tester. Results are shown in Table II. Even at a concentration of 0.1%, dibromomethane reduces the impact sensitivity of benzene and cumene. Similar effects were sought in vinyl chloride (PVC) and a phenolic polymer. Four samples, two containing retardants, were prepared and impact tested: PVC, PVC + 1.5% Sb_2O_3 (a fire retardant), phenolic, and phenolic + 2% tris(2,3-dibromopropyl)phosphate (a retardant). Both PVC samples charred on every test and the phenolic polymers both gave eight positive out of 10 tests. In the case of polyvinyl chloride, the results are not definitive, for fire retardants usually promote charring instead of combustion. The retardant in the phenolic resin appears to be ineffective under the test conditions.

These results indicate that with proper choice of retardant and formulation, improved impact sensitivity of lubricants, sealants, and other materials for LOX application could possibly be obtained.

D. Thermal Ignition Studies

The hot spot theory of ignition served as working hypothesis for the design of impact tests. If it is a valid theory, the relative impact sensitivities of a group of organic compounds as determined by the ABMA tester should reasonably agree with the relative ignitabilities of these same compounds as determined by some other ignition technique. Based upon this assumption, an alternative method of igniting organic samples in LOX was developed during last year's program. This method was referred to as the hot-wire method.

1. Apparatus and Tests

During the present program the hot-wire apparatus was modified and improved to permit accurate measurement of heating rates, ignition temperatures and ignition delay times. It is pictured in Figure 1, and the

Table II

EFFECT OF DIBROMOMETHANE ON IMPACT SENSITIVITIES OF BENZENE AND CUMENE

Formulation Tested	Impact Sensitivity (43", w retainers)
Dibromethane (DBM)	0/10
Benzene	8/10
95% Benzene, 5% DBM	2/10
97% Benzene, 3% DBM	2/10
99% Benzene, 1% DBM	3/10
99.9% Benzene, 0.1% DBM	2/10
Cumene	7/10
95% Cumene, 5% DBM	2/10
99% Cumene, 1% DBM	4/10
99.9% Cumene, 0.1% DBM	3/10

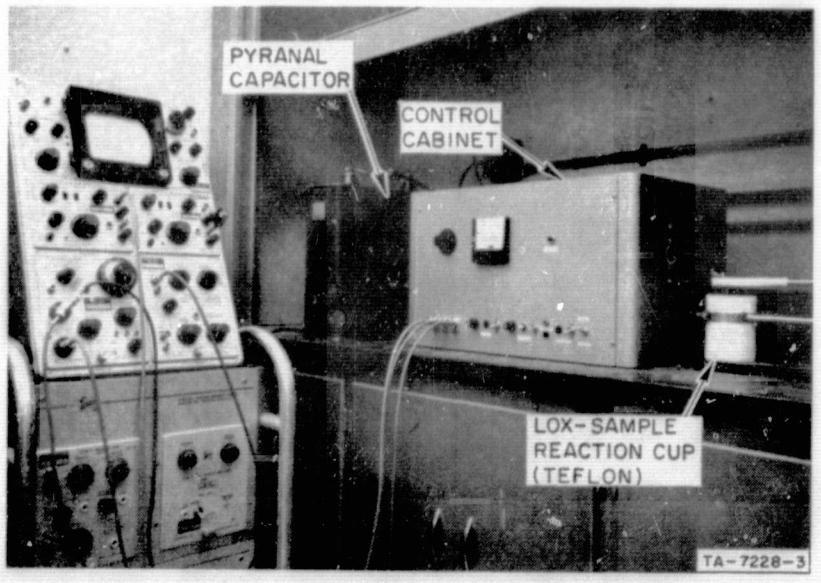


FIGURE 1 HOT WIRE IGNITION APPARATUS

electrical diagram is shown in Figure 2. A 60-μfd capacitor is charged to from 700 to 800 volts, and is then discharged through a 30-gauge platinum resistance wire. This wire, which is one leg of a Wheatstone bridge, is partially immersed in the organic sample held in a small cup. The discharge switch triggers a trace on a Tektronix oscilloscope equipped with a type-W comparator. The trace represents the bridge unbalance, and is therefore a measure of the platinum wire temperature.

Before the hot-wire ignition studies reported herein, the apparatus was calibrated and the sample support apparatus and test technique perfected.

a. Calibration of Hot-Wire Apparatus. The output of the bridge detector circuit in millivolts was determined at several temperatures of the platinum resistance wire, from -196° to 884°C. The 4-cm. platinum loop (Figure 3) was immersed in the calibrating substance and the bridge output then measured with the oscilloscope. The temperatures of calibration are shown in Table III. The bridge output versus platinum wire temperature plots for two different wire resistances are shown in Figure 2. It should be noted that the plot is nonlinear above 300°C and furthermore was extrapolated above the Na_2SO_4 melting point since ignitions occurred at higher hot-wire temperatures.

b. Sample Support Apparatus. Various sample support configurations were tested, and the support shown in Figure 3 was adopted. Capacitor lead posts coming directly from the control cabinet provide the support for the system. These lead posts are slip-fitted into two other brass posts, which hold the platinum wire loop. The 4-cm. platinum wires were supported by first soldering 1/2-in. long x 1/8-in. diameter brass rods to each end of the platinum wire. These small brass rods were then held in place in the larger posts with set screws. The samll glass sample cup shown in detail in Figure 3 is supported by a glass frame.

c. Ignition Tests. An ignition test was run as follows. Approximately 15 μl of the sample was measured into the sample cup. The wire was partially immersed in the sample, after which the sample was frozen around the wire with liquid oxygen. The sample cup and the small brass rods were then immersed in LOX and the discharge was fired.*

*This operation should be carried out behind a safety shield.

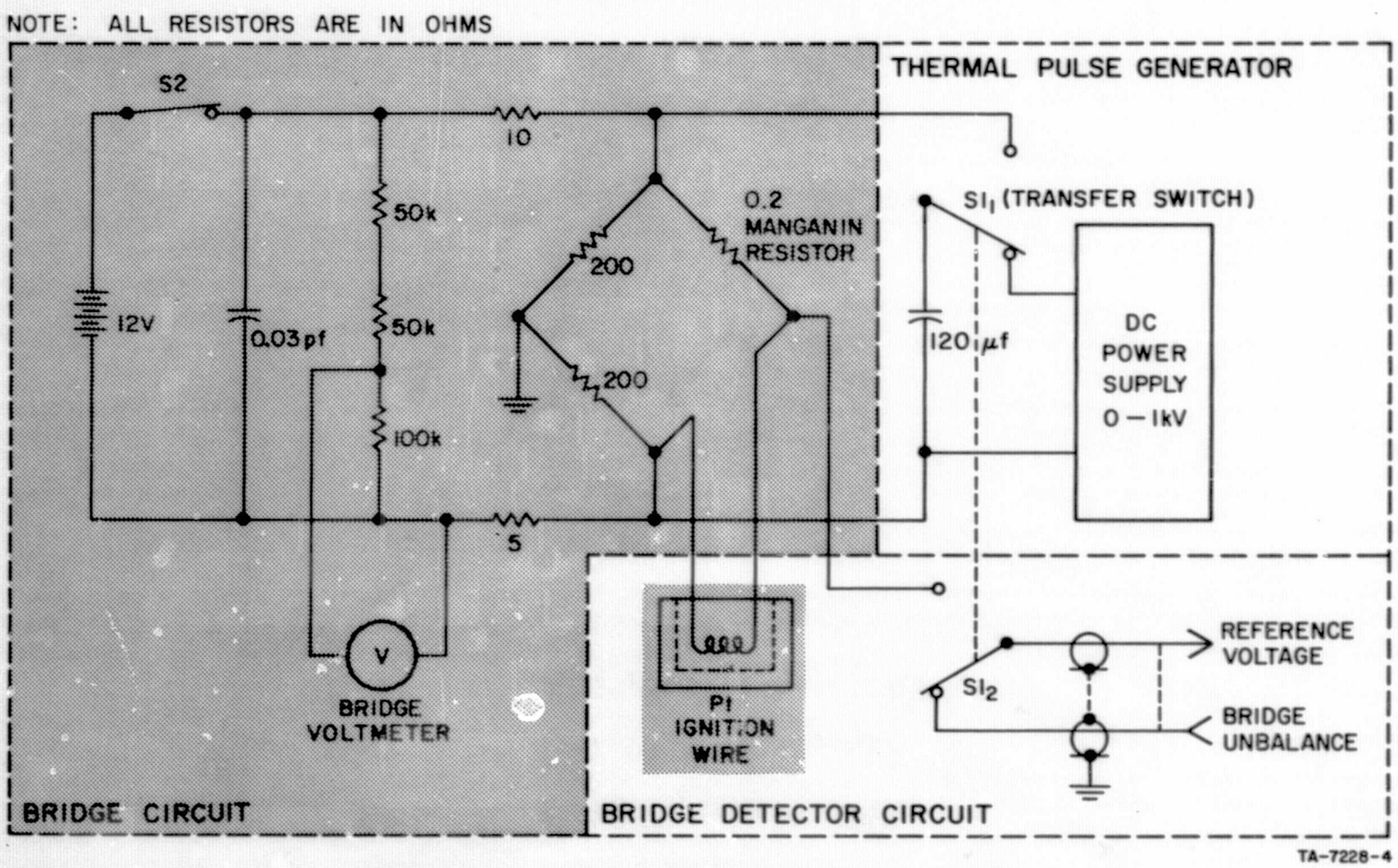


FIGURE 2 HOT WIRE APPARATUS SCHEMATIC DIAGRAM

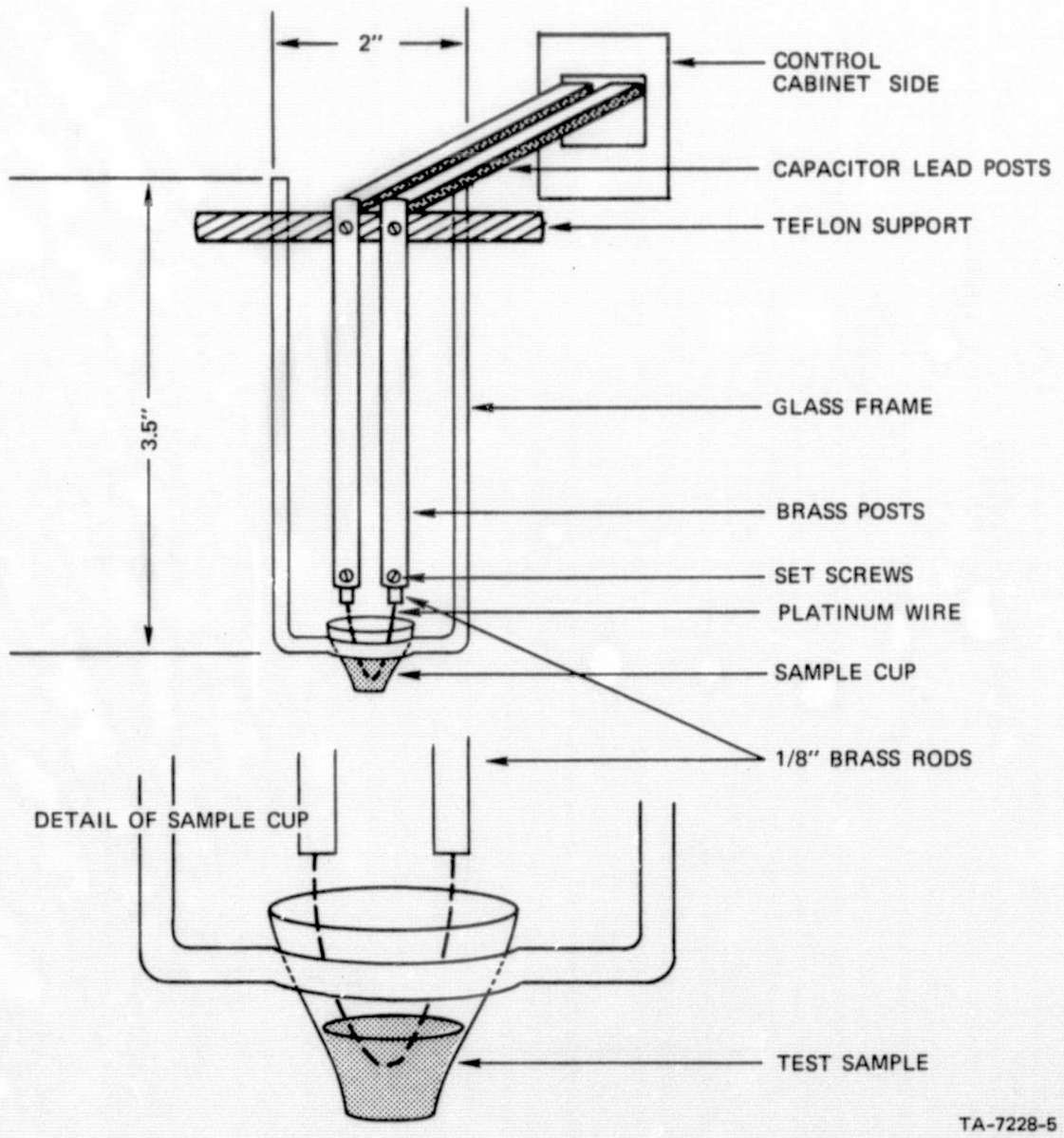


FIGURE 3 SAMPLE SUPPORT APPARATUS

Table III

FIXED TEMPERATURES FOR HOT-WIRE CALIBRATION

Substance	Point	T (^{o}C)
N_2	b. pt.	-196
H_2O	m. pt.	0
H_2O	b. pt.	100
30.5% NaCl 69.5% Na_2SO_4	m. pt.	637
Na_2SO_4	m. pt.	884.7

Ignition test data obtained for benzyl alcohol are shown in Figure 4. Figure 4a represents the temperature profile of the hot wire as it cooled after being pulsed from the capacitor. In this case no ignition occurred. It should be pointed out that the straight portion of the trace and a small extrapolated portion prior to this is a measure of the temperature of the hot wire. The sharply descending initial part of the trace is due to the discharge relay bounce, which is extremely difficult and costly to eliminate.

Figure 4b and 4c are temperature profiles of the platinum wire in samples of benzyl alcohol that did ignite. Figure 5 shows that peak wire temperatures of approximately 1400°C were required to ignite the samples. Comparison of Figure 4a to 4b and 4c provide approximate ignition delay times, τ of 10 to 15 ms.

A few of the same organic compounds that were impact-tested to relate chemical structure and physical properties to sensitivity were ignited in LOX by the hot-wire ignition technique. The minimum ignition temperatures and respective ignition delay times for Series I compounds (benzene, bromobenzene, naphthalene, anthracene, hexane, and cyclohexane) and Series II compounds (isopropyl ether and isopropyl alcohol) are shown in Table IV. Impact-sensitivity data previously reported for these compounds are included for comparison. The ease of ignition was determined by consideration of both the minimum peak temperature required and the length of the ignition delay.

Among the Series I compounds, hexane and cyclohexane were the most sensitive to hot-wire ignition. This same order was also obtained in impact studies and is thought to be related to low flash points of these compounds. Benzene, the most impact-sensitive compound in the group, was measurably less reactive to hot-wire ignition than hexane or cyclohexane, but more easily ignited than its homologs, naphthalene and anthracene. This order of reactivity, benzene > naphthalene > anthracene, is in agreement with the order of reactivity observed in impact tests.

The data for ignition of isopropyl alcohol and isopropyl ether, Series II compounds, by hot wire in LOX has also been studied and the

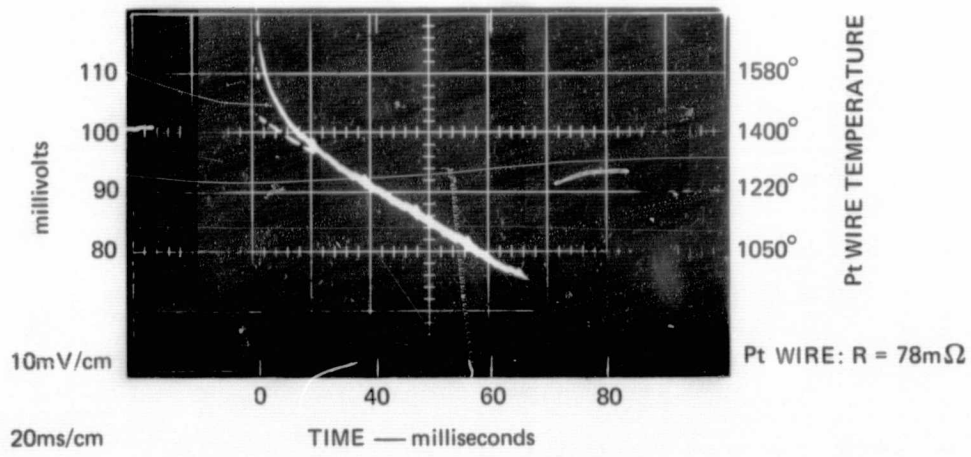


FIGURE 4a NON-IGNITION—blank

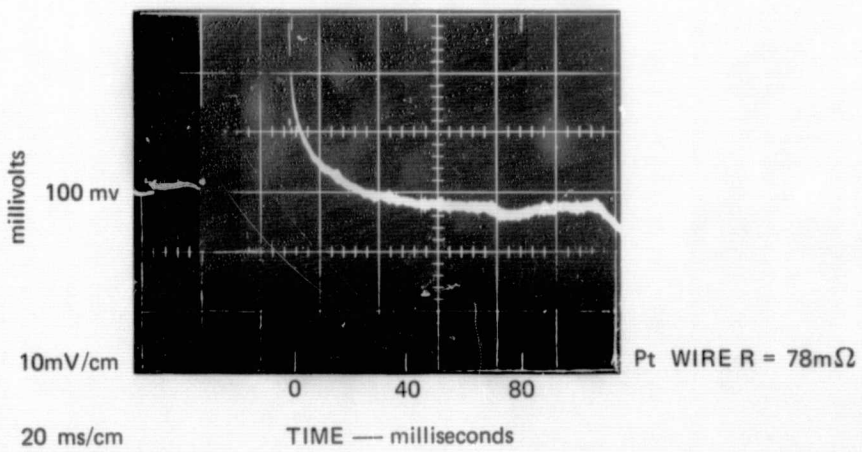


FIGURE 4b IGNITION OF BENZYL ALCOHOL

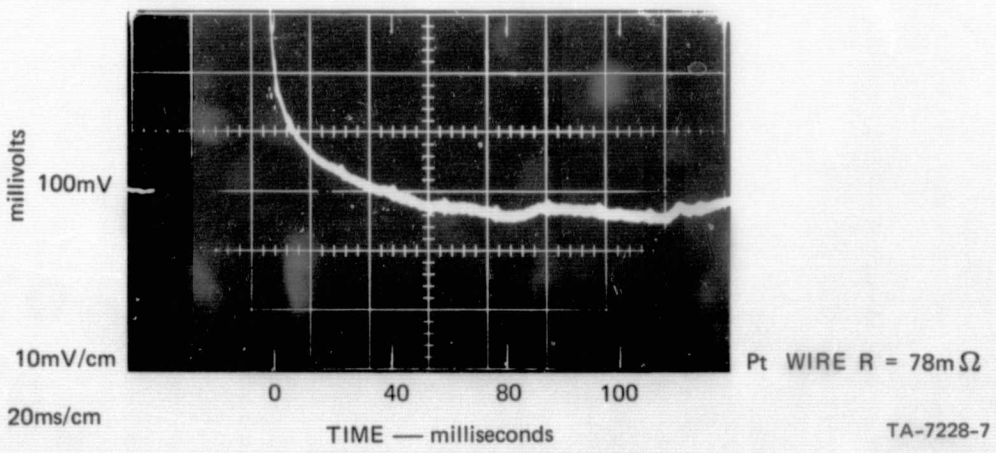


FIGURE 4c IGNITION OF BENZYL ALCOHOL

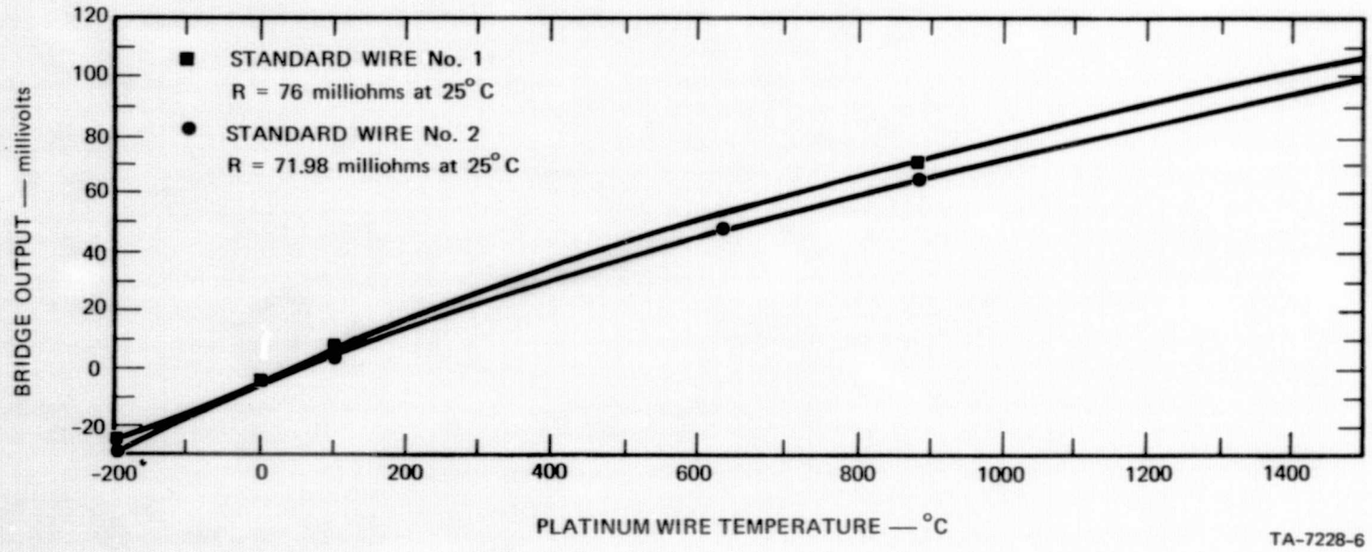


FIGURE 5 PLATINUM WIRE TEMPERATURE VERSUS BRIDGE OUTPUT

Table IV

COMPARISON OF IMPACT AND HOT-WIRE SENSITIVITY DATA

Compound	Thermal Ignition Data		Impact Sensitivity						Physical Properties				
	Peak Temp., °C	τ, ms	Ht., in.	Reactions / Trials	1st	2nd	3rd	Conditions	M.P., °C	B.P., °C	Flash Point, °C	Auto-ignition Temp., °C	ΔH_T
Series I													
Benzene	1380	6	24	6/10	4	2		W/O Retainer	+5.5	80.1	-11	580	124
	1330	12											
	1490	4	43	16/21	15	1		W Retainer					
			43	8/11	7	1		W/O Retainer					
Bromobenzene	1450	4	24	4/10		4		W/O Retainer	-30.6	156	65	688	73.8
	1400	4	43	0/10				W/O Retainer					
	1450	2	43	3/10				W/O Retainer					
Naphthalene	1460	8	24	0/10				W Retainer	80.2	218	79	567	78.9
			43	0/10				W Retainer					
			43	2/10	2			W/O Retainer					
Anthracene	1480	12	24	0/10				W Retainer	218	342	121	472 (O_2)	158
			43	0/10				W Retainer					
			43	0/10				W/O Retainer					
Hexane	1290	4	43	6/10	3	2	1	W Retainer	-94	69	-22	248	124.3
	1220	7.5	43	5/10	4	1		W/O Retainer					
Cyclohexane	1280	11.5	43	4/10		2	2	W Retainer	6.5	80.7	-17		121.8
	1320	10.0	43	3/10		3		W/O Retainer					
Series II													
Isopropyl ether	1390	4.5	43	6/20	2	4		W Retainer	-85.89	69	-28	443	94.5
	1375	8	43	10/20	3	7		W/O Retainer					
Isopropyl alcohol	1270	9	43	3/20		3		W Retainer	-88.5	82.26	11.7-14.5	456	181.6
			43	3/20		3		W/O Retainer					

alcohol ignites at a lower peak temperature. In contrast, the ether was more reactive to impact.

Most of these tests exhibited the inverse relationship between peak temperature and ignition delay time, that is, the higher the peak temperature, the shorter the delay time. The ignition of materials by this technique must occur at the LOX-sample interface in a small volume surrounding the platinum wire. Here, the flammable vapor can be mixed with gaseous oxygen at a temperature high enough to cause ingition. In other words, a rather large hot spot is being created at this point. Furthermore, since the hot-wire studies appear, in most cases, to correlate with impact sensitivity data, the hot spot theory of ignition is given further credence. The apparent importance of the flash point is also emphasized.

E. High-Speed Photography

High-speed photographic studies of impact ignition in explosives[1] supports our hypothesis that the impact ignition of materials in a LOX environment is initiated at a point. We surmise that for brittle materials propagation proceeds along surfaces that are generated by impact.

Our ballistic impact apparatus was fitted with a modified anvil to permit the photography of ignition and propagation events with a high-speed camera. Several preliminary experiments were accomplished. Still photography was used to measure the light from the reaction flash, and to estimate the total sample ignition area. In another experiment the light intensity was measured and two important times determined: (1) the delay time from impact of plummet and striker pin until first light of ignition and (2) the time duration of the flash. Following these preliminary experiments high speed movies of the LOX impact ignition of benzyl alcohol were obtained.

1. Still Photography

Figure 6 shows the modifications made on the impact apparatus to permit photography of impact processes. Still photography was used to qualitatively estimate the amount of light obtained from an impact ignition in LOX, and to observe the extent to which the sample burned.

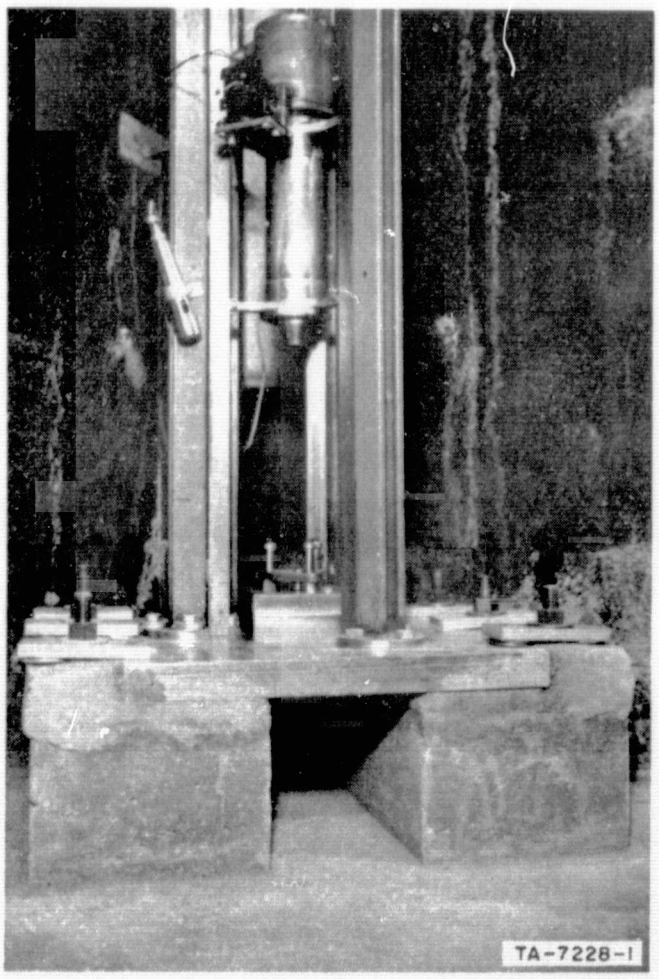


FIGURE 6 DROP-WEIGHT TESTER MODIFIED FOR HIGH SPEED PHOTOGRAPHY

A cross section of the anvil assembly, and the manner in which the combination of two mirrors and one achromatic lens brings the sample plane into visual focus, is shown in Figure 7. A Minolta 101 camera with a 135-mm lens was found appropriate for still photographs. It is equipped with a long shutter release cable so that the shutter can be operated remotely. Tri-X, a fairly sensitive film, was used.

Figure 8 shows the 0.5-in. thick Lexan anvil-cup polished on both ends. A disk was glued into a recess on one end of the anvil cup to provide an 11/16-in. diameter by 0.050-in. thick sample cup.

Benzyl alcohol, which is extremely sensitive to impact was used exclusively in these preliminary studies. In this experiment benzyl alcohol was measured into the Lexan anvil-cup, and the anvil and sample were cooled in the cooling box. Next the sample was positioned for testing, the room darkened, the camera shutter opened, and the plummet released. Following the flash, the shutter was closed. A series of impact ignitions were photographed at shutter openings from f-2.8 to f-22. One taken at f-22 is shown in Figure 9. The dashed white line outlines the sample. This area represents about 0.6 of the sample surface directly under the striker pin. The remainder of the photograph shows light reflected from the cone-shaped walls of the anvil assembly (refer to Figure 7).

Ignition occurred primarily in one central area of the sample and secondarily around the sample edges. Other pictures have shown similar phenomena. Furthermore, all of the photographs taken showed that there was sufficient illumination from reaction flashes to obtain high-speed photographs.

2. Delay Time and Flash Time

When taking high-speed movies of a phenomenon of very short duration the precise time durations of various successive events must be known, as well as the time duration of the entire process. With the impact process, three event-times must be known: (1) drop-time of the plummet, (2) delay time from impact of plummet striker pin until first light emission, and (3) duration of light flash. Only items 2 and 3 were determined since item 1 is well known.

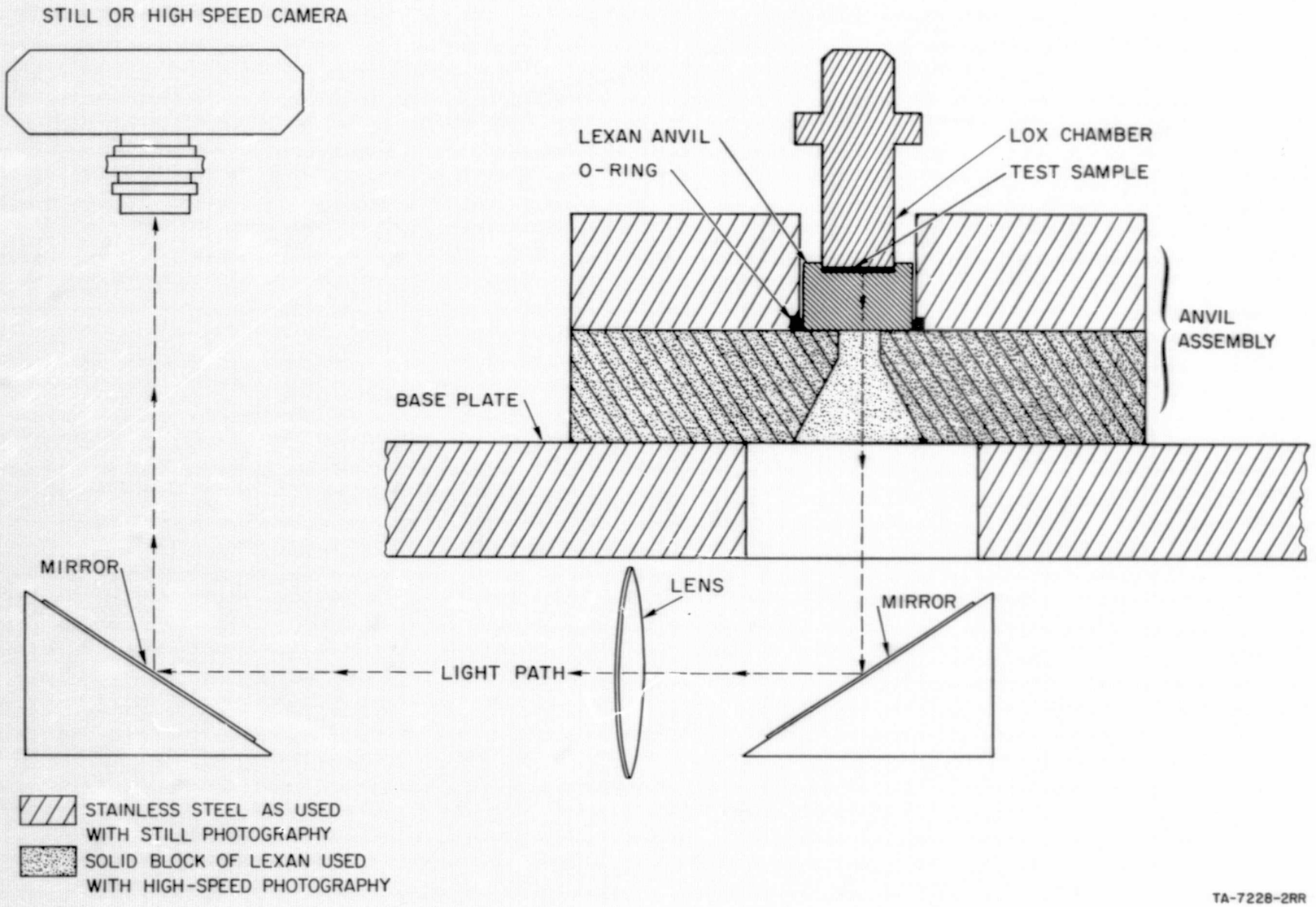


FIGURE 7 CROSS SECTION OF ANVIL ASSEMBLY

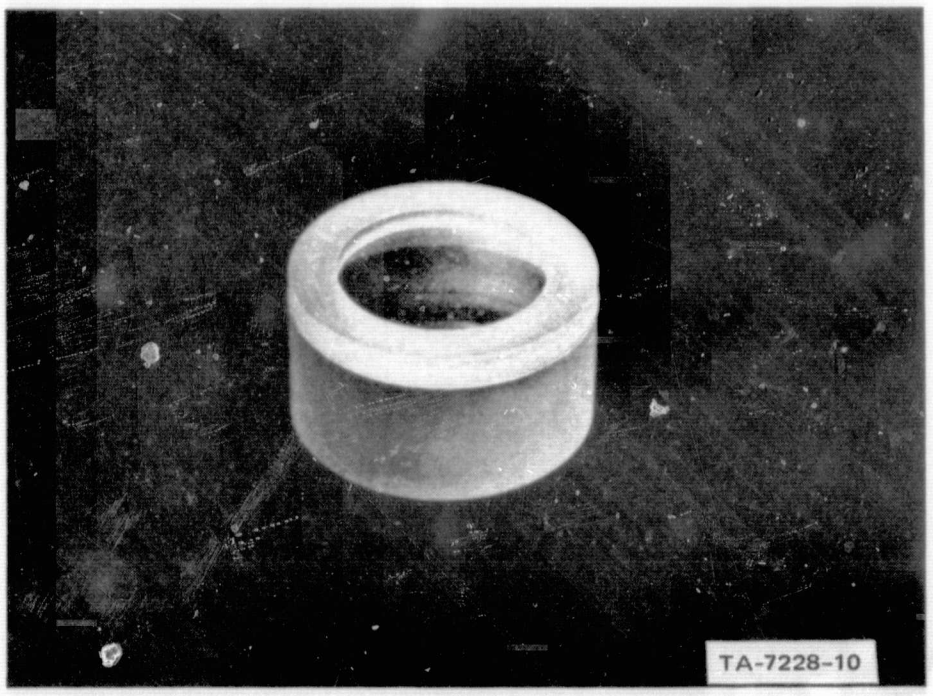


FIGURE 8 LEXAN ANVIL-CUP

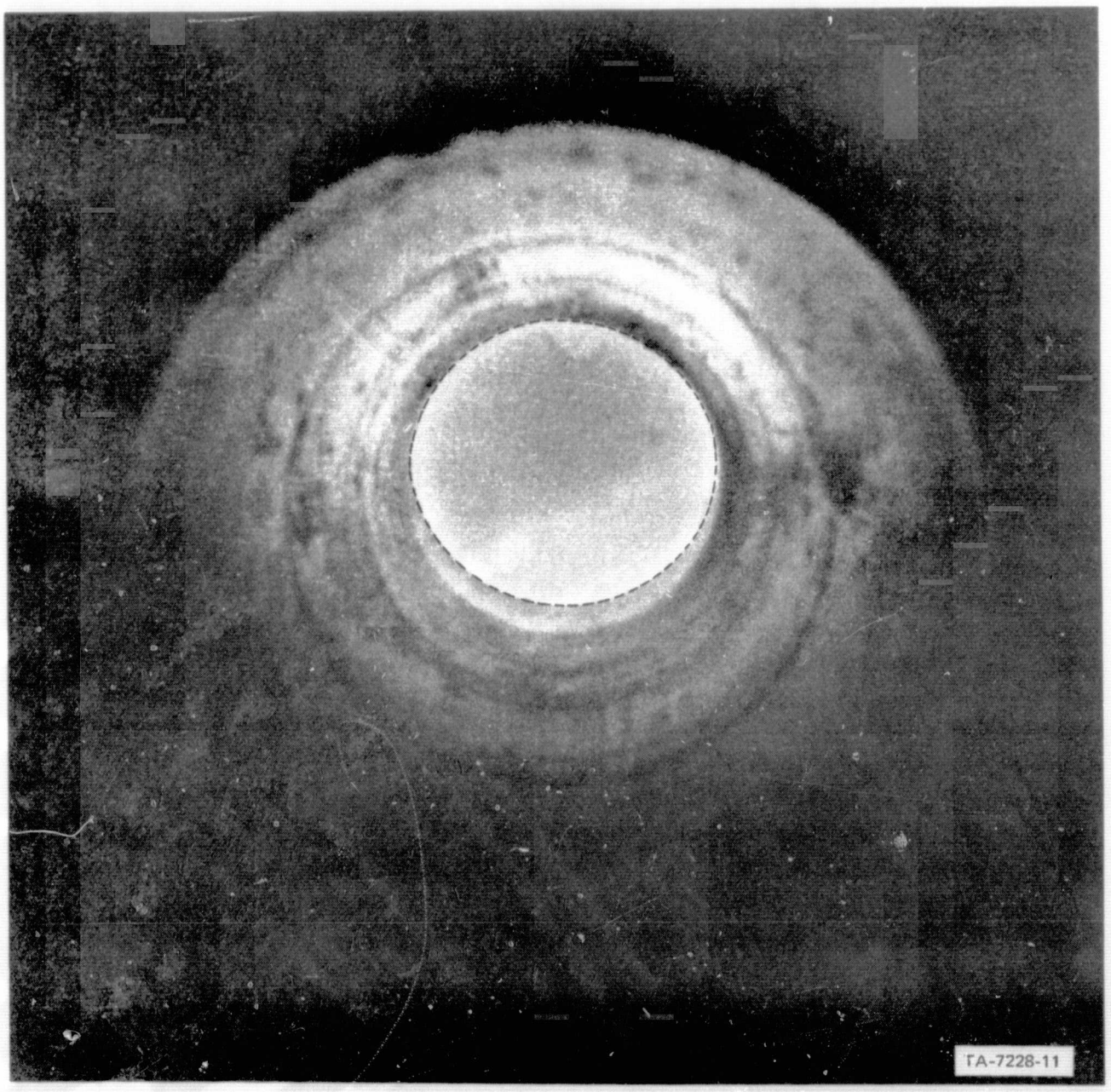


FIGURE 9 STILL PHOTOGRAPH OF REACTION FLASH

Two circuits were used to measure the delay time and flash duration. In one of these a pin-switch circuit triggered a trace in a Tektronix oxcilloscope when the plummet impacted the striker pin. The light emitted by the igniting sample was detected with a pin photodiode mounted directly under the Lexan anvil. This photodiode (H.P. 4203) is sensitive to ir, uv, and visible radiation and has an output of about 250 mv at 210,000 candle power.

In the second circuit, a second scope was triggered by the flash itself. Figures 10a and 10b show traces obtained when both circuits were used simultaneously. The sample, benzyl alcohol, exhibits a delay time of 480 μsec, a flash duration of about 500 μsecs, and a peak intensity of about 190,000 candle power. Other traces show delay times ranging from 250 to 550 μsec and flash durations varying from 200 to 700 μsec. They also showed that sufficient illumination was available for high-speed photographs.

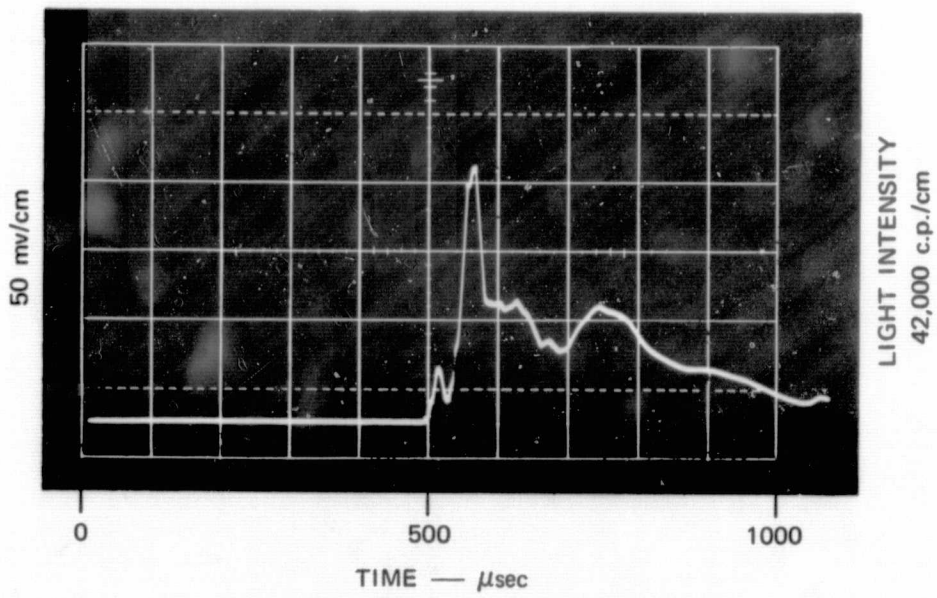
The flash durations are obviously quite short and necessitate the use of very high framing rates in order to obtain an informative sequence of pictures.

3. High-Speed Photographs

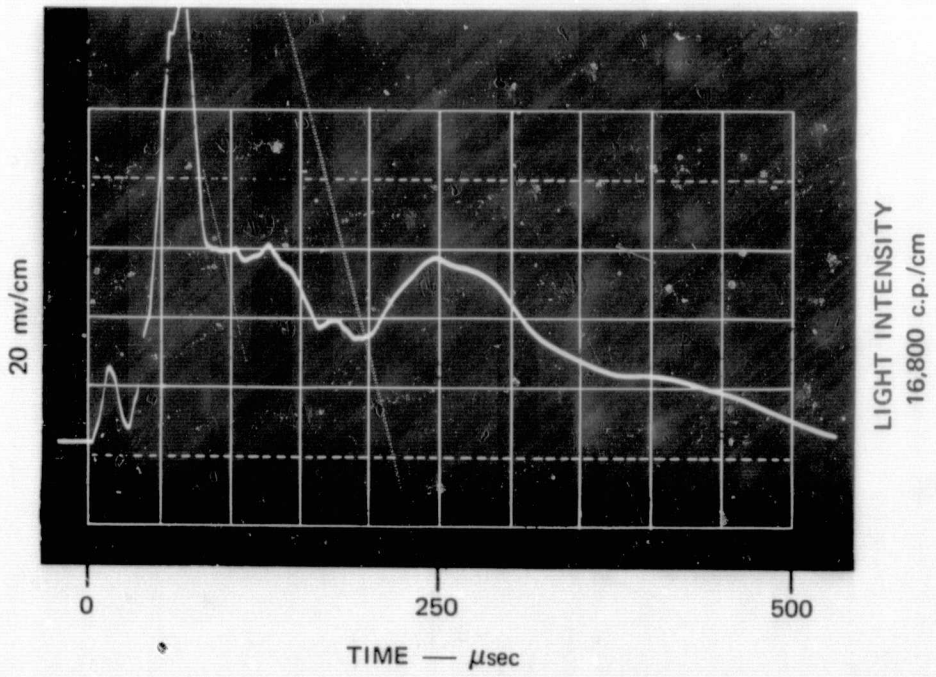
High-speed movies of the impact ignition of benzyl alcohol in LOX were prepared. The photographic equipment consisted of a Hycam 2 camera with Tri-X film. This 16-mm camera is capable of speeds up to 7000 frames per second and will yield 14,000 pictures per second when half frame exposures are utilized.

The anvil assembly used for still photography was improved for high-speed photography by replacing the stainless steel anvil on which the Lexan anvil-cup rested with a 5-in. square x 1-in. thick plate of transparent Lexan. This provided a clear uninhibited view of the entire sample since the cone-shaped cavity was eliminated.

Filming a LOX impact was a relatively simple operation. Following the placement of anvil cup and striker pin in proper positions, the plummet release switch and camera start switch were activated simultaneously



(a) IMPACT TRIGGERED TRACE



(b) LIGHT TRIGGERED TRACE

TA-7228-12

FIGURE 10 TRIGGERED TRACES OF REACTION FLASH

from a remote location. When impact occurred, approximately 500 msecs later, top film speed of 7000 frames per second was attained (14,000 pictures per second).

Four high-speed movies showing the impact ignition of benzyl alcohol were taken, two at 3500 half-frames (7000 pictures) per second and two at 7,000 half-frames or 14,000 pictures per second.

Several frames of film number three are shown in Figure 11. The outer dashed line shows the border of the sample wafer, while the inner dashed line indicates the area impacted by the striker pin. These frames show that benzyl alcohol ignition first occurs at a point under the striker pin (pictures 1-3) followed by ignition at the edges of the striker pin (pictures 6 and 7), and propagation into the uncompressed sample surrounding the striker pin (pictures 8-11). (The light emanating from outside the sample area dashed line is reflected light from sample combustion. This same general phenomenon occurs inthe other high-speed movies.) These movies provide convincing evidence that ignition can initiate from point sources (hot spots) that result from impact. The movies also provide evidence that, once ignition has taken place in a LOX environment, propagation within this environment can occur, the extent probably depending upon the physical and chemical properties of the tested compounds.

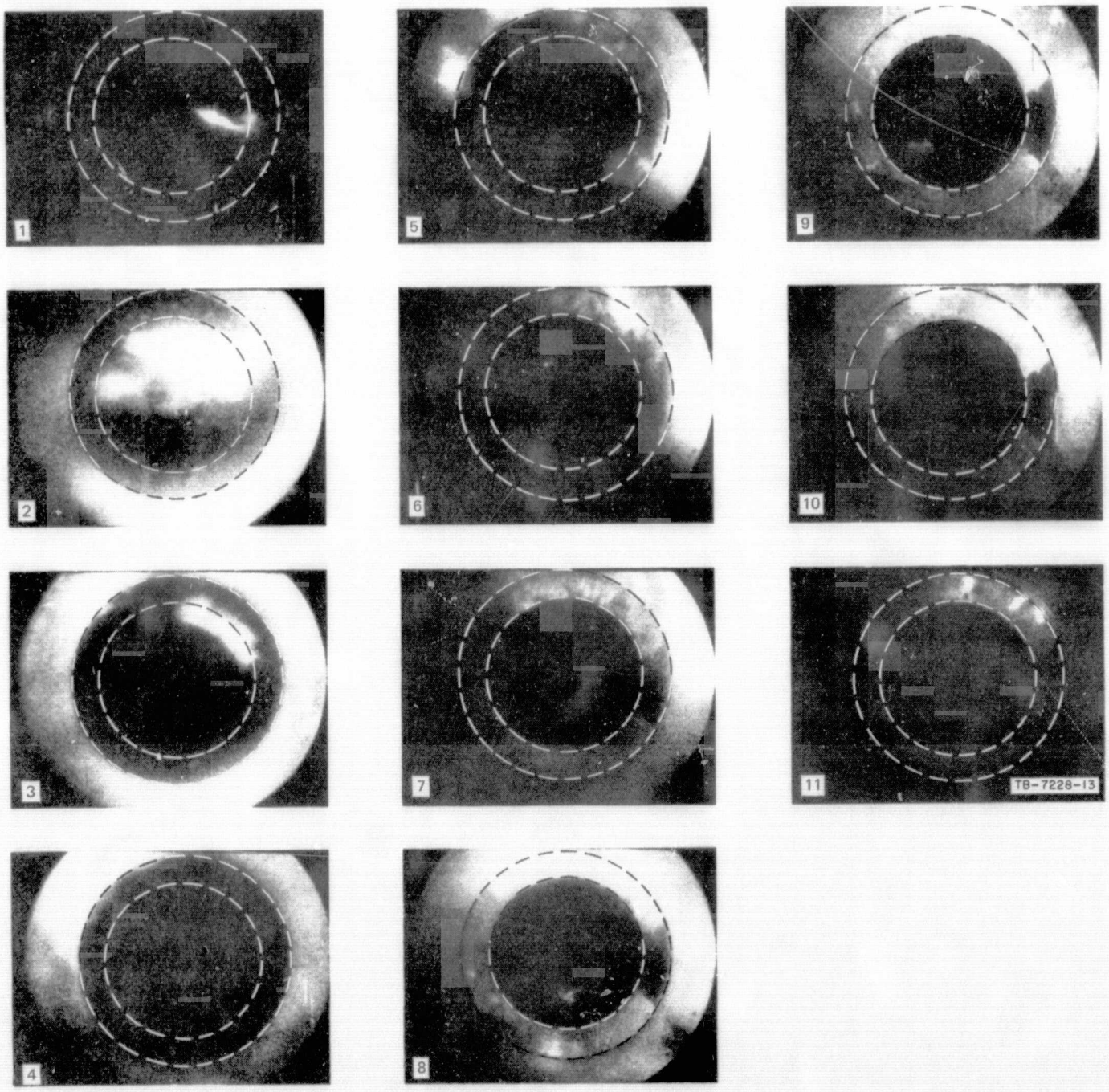


FIGURE 11 IMPACT IGNITION AND PROPAGATION OF BENZYL ALCOHOL IN LIQUID OXYGEN

III OXIDATION MECHANISMS FOR ORGANIC COMPOUNDS

A. Background

Our present understanding of impact sensitivity processes suggests that deflagration of organic compounds in LOX takes place at elevated temperatures where production of free radicals is fast and where several kinds of exothermic autoxidation processes become important. The relative sensitivity of materials must be a function of both physical and chemical properties, the former governing how the initial mechanical energy is converted to heat and the latter controlling the rate of oxidation. In order to develop useful structure-sensitivity relationships we need to know how these properties contribute separately to the overall effect. This part of the program has been concerned with measurements of the relative reactivity of selected organic compounds towards peroxy and alkoxy radicals under mild conditions in dilute solution where physical properties should have little or no effect. The temperatures encountered in the combustion regime, although much higher than used in these experiments, probably alters only the proportions--not the kinds of radicals, and compresses the range of selectivities as measured at lower temperatures.

Impact measurements on these same and other organic compounds were reported in Section II, and provide the basis for estimating the relative importance of physical and chemical properties in the complex impact phenomena.

Since even simple oxidation reactions involve several competing radical processes, each of which may be sensitive to changes in structure, it is experimentally difficult to determine structure-reactivity relationships for diverse classes of organic compounds. For this reason, we have also investigated the relative reactivity of these same compounds towards t-butoxy radical under conditions similar to those used for the oxidations. Our interest in t-BuO· radical stems from some unpublished results in our laboratory that indicate the t-butoxy and peroxy radicals (chain carriers in oxidation) have about the same selectivity towards

hydrocarbons. If this similarity extends to other classes of organic compounds, then we have the basis for an experimentally simple procedure for estimating relative reactivity in oxidation.

In addition, we have investigated the oxidation of trimethylaluminum as an example of the low temperature spontaneous reaction of oxygen with certain classes of organic compounds. To complete some earlier work,[1] we also examined the oxidation of $CF_3\cdot$ radical at low temperatures.

B. Summary

We have investigated the relative reactivity of several classes of organic compounds toward t-butoxy and t-butyl peroxy radicals at 50 and 100°, mostly in benzene solvent. Tertiary-butoxy radical was generated photochemically at 50 and thermally at 100° using t-Bu_2O_2. Relative rates of abstraction versus cleavage of the t-BuO· radical were measured for five hydrocarbons, five benzyl derivatives and nine aliphatic derivatives. At 100°, the ratio of abstraction from tertiary, secondary and primary CH bonds in hydrocarbons is 54:7:1. Little difference was noted in the high relative reactivity of several benzyl compounds, benzyl resonance effects being predominant. A wide range of reactivity was found for the aliphatic compounds with over a 100-fold difference found between reactive acetaldehyde and almost inert isopropyl acetate.

Relative rates of oxidation for four aliphatic compounds were measured in the presence of t-BuO_2H to convert all peroxy radicals to t-$BuO_2\cdot$ radical and permit comparisons of the relative rates of propagation. At 50°, i-Pr_2O, i-Pr_2CO, and Et_2O all react at the same rate (on a per hydrogen basis) and are five times more reactive than isobutane. At 100°, i-Pr_2O and i-PrOH are about equally reactive and are about twice as reactive as isobutane but about one thousand times as reactive as inert isopropyl acetate.

Although the trends for reactivity toward t-BuO· and t-$BuO_2\cdot$ radicals are similar, the correlation is qualitative at best among compounds with diverse structures. There appears to be little correlation between reactivity in oxidation and impact sensitivity; volatility as reflected

in flash points appears to be of greater importance with most compounds tested.

The oxidation of Me_6Al_2 at -140 to 100° in CF_2Cl_2 or $CFCl_3$ is very fast, with a specific rate constant of 10^{-2} to 10^{-3} l/mol sec. The intermediate $MeOOAlMe_5$ rearranges rapidly around -100° to form $(MeO)_2AlMe_4$. A displacement of oxygen on the dimer seems to account best for the chemical and kinetic requirements of the system. A brief study of the addition of methanol to Me_6Al_2 indicates that the mechanism and the final products are similar to those for oxygenation.

In completing an earlier investigation of the oxidation of CF_3 radical at -100°, we photolyzed hexafluoroazomethane in $CFCl_3$ in the presence of oxygen. No oxygen evolution was noted from the reaction mixture, but nmr spectra indicated the presence of some $CF_3O_3CF_3$ and possibly some $CF_3O_4CF_3$. Considerable CF_2O and SiF_4 were also formed by an unknown mechanism.

C. Relative Rates of Oxidation (t-$BuO_2\cdot$ Radical)

Most free radical oxidation reactions involve peroxy radicals[5] at temperatures up to 200°C. A general scheme for autoxidations may be expressed in the following steps

1. $X_2 \xrightarrow{k_i} 2X\cdot$ $\qquad R_i = k_i(X_2)$
2. $X\cdot + RH \longrightarrow XH + R\cdot$
3. $R\cdot + O_2 \xrightarrow{\text{fast}} RO_2\cdot$
4. $RO_2\cdot + RH \xrightarrow{k_p} RO_2H + R\cdot$
5. $2RO_2\cdot \xrightarrow{k_t} (2RO\cdot)_{\text{cage}} + O_2$
6. $(2RO\cdot)_{\text{cage}} \xrightarrow{ak_t}$ Termination
7. $RO\cdot + RH \xrightarrow{\text{fast}} ROH + R\cdot$

Here, both $RO\cdot$ and $RO_2\cdot$ are chain carriers and both are involved in termination. The rate of oxygen uptake can be shown* to follow the relation

*The derivation assumes all radicals are in steady state and $R_i = R_t$

$$R_o = R_i^{\frac{1}{2}}(k_p/2k_t^{\frac{1}{2}})(RH) + \frac{R_i}{2a} \qquad (1)$$

It should be possible to establish a relationship between changes in k_p and changes in RH, providing R_i, k_t and a remain constant. Unfortunately this is rarely the case. The usual experimental procedure is to measure R_o, keeping R_i constant by adding a free radical initiator such as peroxide or azo compound, and evaluate $k_p/2k_t^{\frac{1}{2}}$ from Equation 1. However, because k_t also changes comparisons of k_p alone for a series of compounds are not directly obtainable except by special techniques such as epr[6] or rotating sector.[7] Oxidations of mixture of compounds is also used to obtain relative values of k_p; however, the experimental procedures are laborious and the results often inaccurate without unusual experimental effort.

Several years ago Howard and coworkers[3] observed that peroxy radicals abstract from hydroperoxides very rapidly

$$R'O_2\cdot + RO_2H \rightleftarrows R'O_2H + RO_2\cdot$$

Thus, by adding about 0.2-0.5 M $C_6H_5CMe_2O_2H$ to an oxidation reaction, all peroxy and alkoxy radicals are converted to $C_6H_5CMe_2O_2\cdot$. This greatly simplifies measurements of relative reactivity in oxidation since all propagation and termination steps now involve only one kind of peroxy radical and, because k_t always refers to the same termination reaction involving caged alkoxy radicals, comparisons of $k_p/2k_t^{\frac{1}{2}}$ gives k_p for different compounds directly. We have used this procedure to measure the relative rates of oxidation of four compounds, initially at 100° then at 50°. Experiments were done with isopropyl alcohol, diisopropyl ether, diethyl ether, and diisopropyl ketone in benzene solvent with added initiator (t-Bu_2O_2 at 100° and ABN at 50°) and with ~0.3 M t-BuO_2H. Experiments without hydroperoxide and without added initiator were also done to check the effect of the hydroperoxide. The results are summarized in Table V. The rate equation (1) is changed to

$$R_o = R_i^{\frac{1}{2}} k_p (2k_t)^{\frac{1}{2}}[RH] - R_i/2a \qquad (2)$$

Table V

RELATIVE REACTIVITIES OF ORGANIC COMPOUNDS TOWARD t-BuO_2· RADICALS IN BENZENE
(Concentrations in M, rates in M/min)

RH	Conc.	$[t\text{-}BuO_2H]_o$	Initiator	$R_o \times 10^6$	R_i[a] $\times 10^6$	$k_p/(2k_t)^{\frac{1}{2}} \times 10^2$[b]	Rel. k_p per CH	t-BuO· Radicals	
								k_a/k_d[c]	Rel. k_a per CH
50°, ABN initiator									
i-Pr_2O	2.8	0.29	0	0	0			-	
i-Pr_2O	3.77	0.29	0.0484	185	7.38	1.4	3	0.74	0.05
i-Pr_2O	4.01	0	0.0516	77	7.85	-		-	
Et_2O	3.85	0.31	0	80	-	-		-	
Et_2O	3.7	0.32	0.0447	325	4.90	3.61	4	16	0.8
Et_2O	4.0	0	0.0486	59	7.41	-			
i-Pr_2CO	3.81	0.35	0.0482	221	7.40	2.4	5.2	2.9	2.2
i-Pr_2CO	3.72	0	0.0528	60	7.8	-		-	
i-BuH	4.99[d]	0	0.0098	17.7	1.2	0.23	1.0	6.7	1.0
100°, t-Bu_2O_2 initiator									
i-Pr_2O	0.92	0.36	0.043	208	3.46	17	2.3	0.1-0.15[e]	0.1
i-Pr_2O	0.99	0	0.042	68	3.46	-			
i-PrOH	0.93	0.29	0.039	79	3.18	6.7	1.9	4.0[f]	3.0
i-PrOAc	7.4	0	0.050	<1	4.2	<.004	<.001	<0.07[e]	<0.055
i-BuH	4.30[d]	0	0.0026	71	0.21	3.6	1.0	1.5[d]	1.0

[a] At 50° $R_i = 1.2k_d[ABN]$ where $k_d = 1.30 \times 10^{-4}$/min (D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, J. Amer. Chem. Soc., 87, 4832 (1965)). At 100° $R_i = 2k_d(t\text{-}Bu_2O_2)$ where $k_d = 4.08 \times 10^{-5}$/min.

[b] $(l/mole/min)^{\frac{1}{2}}$ per molecule.

[c] l/mole per molecule.

[d] Oxidized in CCl_4 solvent; D. Allara, T. Mill, D. G. Hendry, and F. R. Mayo, Adv. Chem. Ser., 76, 40 (1968).

[e] Measured in neat solution.

[f] Estimated for value of sec-BuOH, see Table VIII.

and was used to evaluate $k_p/(2k_t)^{\frac{1}{2}}$ for these reactions, where a = 0.1.

Unfortunately we have found several difficulties with the use of added t-BuO_2H in these systems. At 100°, blank runs without initiator (not shown) indicate there is a significant amount of initiation by the hydroperoxide, which leads to error in the calculated rates of initiation based on t-Bu_2O_2. At 50°, there should be no contribution from thermal decomposition of t-BuO_2H. However, in run 33 with Et_2O, there is significant oxidation in the absence of ABN, indicating there is some molecular initiation reaction involving both the hydroperoxide and ether. No reaction occurs with i-Pr_2O and t-BuO_2H run. The values for $k_p/2k_t^{\frac{1}{2}}$ in Table V are corrected for the small contribution of hydroperoxide to initiation. Because of these unexpected complications, measurements of relative rates of oxidation were not extended to other compounds.

Discussion of the kinetic results is deferred to Section E.

Analyses for products were done first, by titration for hydroperoxide and then by glc after treatment of the reaction mixtures with triphenylphosphine to reduce the hydroperoxides to alcohols[8]. The results indicate that the oxidations proceeded in the following way

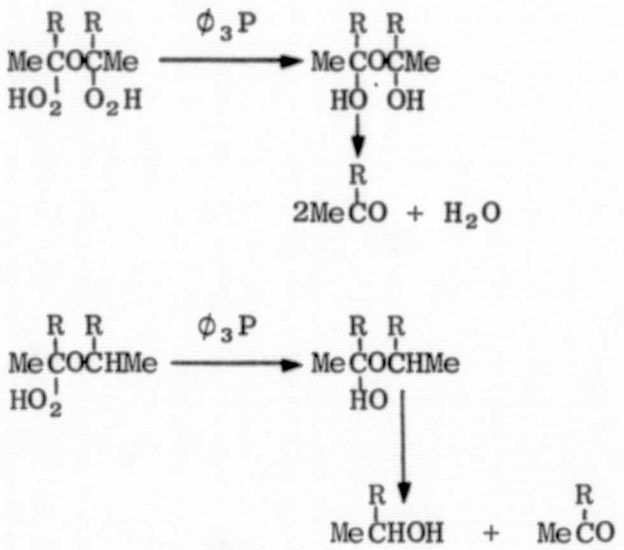
$$\text{i-PrOH} \xrightarrow[100^\circ]{\frac{1}{2}O_2} Me_2CO + H_2O$$

$$\text{i-}Pr_2O \xrightarrow[100^\circ \text{ or } 50^\circ]{O_2} Me_2C(O_2H)CHMe_2 + ME_2C(HO_2)COCMe_2(O_2H)$$

$$Et_2O \xrightarrow[50^\circ]{O_2} MeCH(HO_2)OCH_2Me + MeCH(HO_2)OCHMe(O_2H)$$

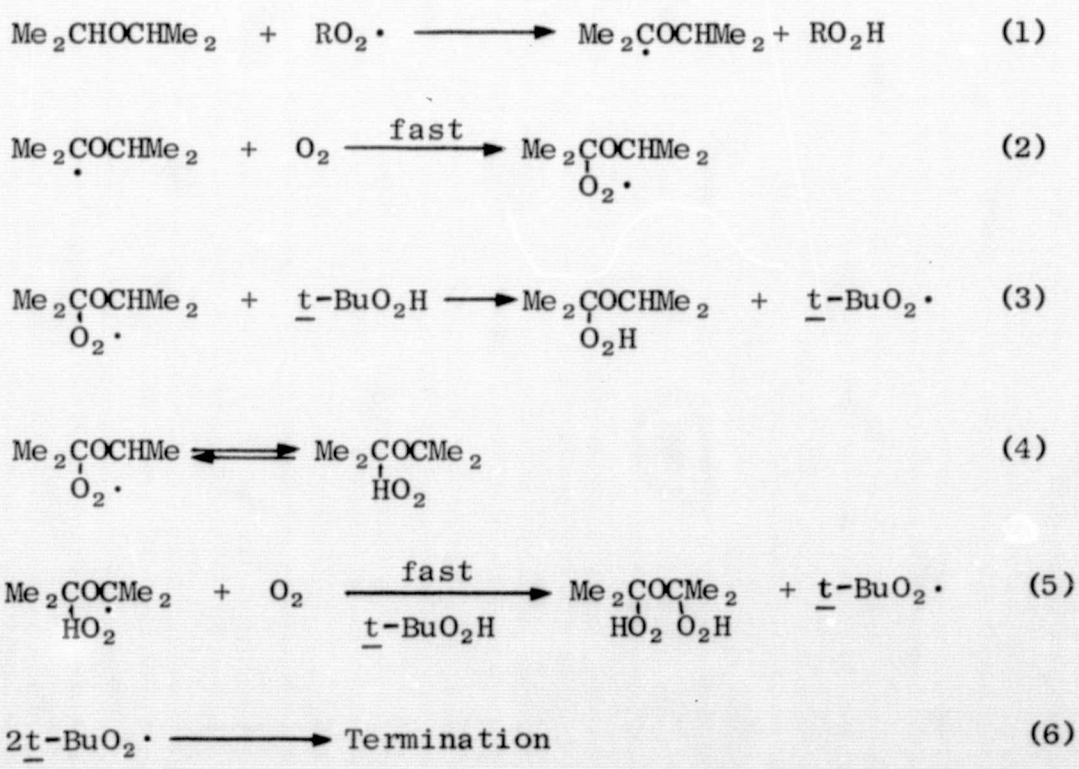
$$\text{i-PrCO} \xrightarrow[50^\circ]{O_2} Me_2C(O_2H)COCHMe_2 + Me_2C(O_2H)CO(O_2H)CMe_2$$

Reduction of the ether hydroperoxides gave unstable hemiketals or acetals that decomposed to the corresponding alcohol and carbonyl compound:



(R = Me or H)

The oxidation of i-Pr_2O and Et_2O gave mixtures of carbonyl and alcohol products in the ratio of ~1:1 to 2:1 in the presence of t-BuO_2H but gave much less alcohol than carbonyl in the absence of t-BuO_2H·. The following scheme for the detailed oxidation of i-Pr_2O (which applies equally to Et_2O) accounts for these results:



If reaction 3 is fast enough to compete with reaction 4, most of the product will be monohydroperoxide and, in the absence of added t-BuO_2H, most of the reaction will proceed via reactions 4 and 5, consistent with our findings.

The oxidation of diisopropyl ketone must follow a scheme similar to that for the ethers except that both the mono and dihydroxy compounds formed on reduction of the corresponding hydroperoxides are stable and could be isolated by glc.

The product balances are in only fair agreement with the ΔO_2 values, particularly in run 31 where more MeCHO was formed than can be accounted for by ΔO_2. Here, some additional reaction not requiring oxidation must give MeCHO.

D. Relative Reactivity Towards t-Butoxy Radical

Alkoxy radicals are often important chain carriers in oxidation reactions, particularly at higher temperatures and in the gas phase where the competition between reaction 4 and reactions 5 and 7 favor the latter sequence. For this and other reasons, there has been considerable interest in the reactivity of alkoxy radicals towards a variety of organic compounds. Unlike oxidation systems, relative reactivity measurements for alkoxy radicals are relatively easy to obtain for two reasons. One is that alkoxy radicals and particularly t-butoxy are easily generated over a wide temperature range from hypochlorites,[9] peroxyoxalates,[10] and peroxides.[11] Second, relative rates of abstraction may be measured directly against the unimolecular cleavage of the alkoxy radical to carbonyl and alkyl radical. The latter reactions is independent of substrate thus providing a simple direct comparison of k_a for different compounds. In the specific case of t-BuO· radical, the two products of interest are t-BuOH and acetone.

$$\text{t-BuO}\cdot + \text{RH} \rightarrow \text{t-BuOH} + \text{R}\cdot \qquad (1)$$

$$\text{t-BuO}\cdot \rightarrow \text{Me}_2\text{CO} + \text{Me}\cdot \qquad (2)$$

The ratio of products at small conversions of RH gives the ratio k_a/k_d directly

$$k_a/k_d = \frac{(\text{t-BuOH})}{\text{Me}_2\text{CO}} \frac{1}{(\text{RH})_o} \qquad (3)$$

Significant solvent effects are noted for this ratio and are attributed to effects on reaction 2 rather than 1; solvents of increasing polarity enhancing cleavage thus decreasing the ratio. It is also clear from Equation 4 that any reaction of substrate RH or its derivative radical that gives either acetone or alcohol would lead to erroneous values of k_a/k_d. Furthermore, formation of a product that is much more reactive than RH would also lead to erroneously high values for k_a/k_d at moderate conversions. To avoid such effects, we have carried out a series of experiments with a variety of aromatic and aliphatic compounds at 50° and at 100° using benzene as a common solvent in most cases and with moderately low concentrations of substrate. Tertiary-butyl peroxide was used as the thermal source of t-BuO· radicals at 100° and as a photolytic source at 50°, where attempts to use the thermal initiator di-t-butylperoxy oxalate (DBPO) failed because of chain reactions between DBPO and the ether substrates.

Benzene also reacts with t-BuO· radical to give some alcohol, requiring a correction to product measurements. In a few cases of very unreactive substrates, the solvent correction gave values of k_a/k_d nearly equal to zero and measurements on these compounds had to be done in neat solution (without benzene solvent). Some experiments at 50° were done using three concentrations of substrate; each experimentally determined product ratio was plotted against the concentration of substrate and the value of k_a/k_d was obtained from the slope of the line. This procedure avoids uncertainties in the value of the correction factor for solvent which might depend on the rate of initiation, a changing and uncertain value in the photolytic experiments. The experimental results are presented in three tables. The first two summarize data at 100° on hydrocarbons and benzyl derivatives and the third summarizes data at 100° and 50° for aliphatic derivatives. Table VI presents heretofore unpublished results on several neat hydrocarbons and indicates that the relative reactivities of primary, secondary, and tertiary C-H bonds towards t-BuO· radical are in the order 1:7:54 respectively. These relative rates are similar to those observed by others at 40°[9] and 135°[12] and are consistent with the generally accepted idea of increasing radical stability with increasing alkyl substitution

Table VI

RELATIVE REACTIVITY OF NEAT HYDROCARBONS
TOWARD t-BuO· RADICAL AT 100°

RH	k_a/k_d per molecule	k_a/k_d per C-H	
i-BuH	1.5	1.3	3°
$Me_2CHCH_2CH_3$	1.8	1.3	3°
$Me_2CHCH_2CHMe_2$	1.4	0.55	3°
n-BuH	0.72	0.14	2°
CMe_4	0.29	0.024	1°

Table VII

RELATIVE REACTIVITY OF BENZYL DERIVATIVES
TOWARD t-BuO· RADICAL IN BENZENE AT 100°

RH	[RH], M	k_a/k_d [a]
BzOH	0.46	8.9
BzOAc	0.47	5.8
BzOMe	0.46	8.2
$BzNH_2$	0.49	183
$BzNMe_2$	0.47	12

[a] Corrected for contribution by benzene solvent to k_a/k_d of 0.081 l/mole.

Table VIII

RELATIVE REACTIVITY OF ALIPHATIC COMPOUNDS
TOWARD t-BuO· RADICAL IN BENZENE

RH	[RH], M 50°	k_a/k_d [a] 50°	[RH], M 100°	k_a/k_d [b] 100°
AcH	--		0.98	89
Et_2O	2.56	16	2	2.8
i-PrOH	0.97	1.3	0.49	1.5
i-PrOAc	1.86	0.23[c]	7.82	0.068
EtOAc	0.18-1.25	0.41		
$i\text{-}Pr_2O$	1.72	0.74	.186	0.2
$i\text{-}Pr_2CO$	0.51	2.9	--	
t-BuH	0.20-1.6	6.7[c]		
sec-BuOH	0.82	19	--	--
t-$BuNH_2$	--		0.64	4.3

[a] Corrected for contribution by benzene solvent to k_a/k_d of 0.24 l/mole.

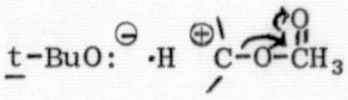
[b] Corrected for contribution by benzene solvent to k_a/k_d of 0.081 l/mole.

[c] From plot of [ROH]/[Acetone] vs [RH]. No solvent correction used.

at the carbon radical and parallel the observed reactivity of these hydrocarbons towards peroxy radical.[13]

The reactivity of the benzyl derivatives in benzene are all high and relatively similar, with the outstanding exception of the benzylamine (Table VII). The remarkable reactivity of this compound is clearly due to the reactive N-H bonds rather than any inductive effect on the neighboring C-H bonds, since the N,N-dimethylbenzylamine has unexceptional reactivity compared to other compounds in the table. In general, the high reactivity of these compounds reflects the benzyl resonance stabilization of the radical rather than any substituent effects.

This conclusion is supported by results shown in Table VIII in which several aliphatic compounds bearing substituents similar to those in Table VII show markedly different reactivities. In particular, i-PrOH and i-PrOAc differ by a factor of 20 in reactivity. This large difference is not due to the presence of the strongly bonded OH hydrogen; rather, it must reflect an unfavorable charge-separated transition state for abstraction from the α C-H of the ester compared to that for the alcohol.



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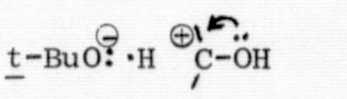


stabilized

Unpublished results from another laboratory[14] indicate that although the bond strength for an alcohol C-H bond is about 90 kcal/mole, the value increases to about 94 kcal/mole in the corresponding ester.

The experiments with ethylacetate serve as a check on the value for isopropyl acetate and on the unlikely possibility that the ester gives some acetone through cleavage of the $\cdot CMe_2OAc$ radical; since the value for EtOAc is just twice that for i-PrOAc, the low values associated with these esters are real and largely a function of the neighboring OAc group.

Just the opposite must be true for $i\text{-}Pr_2O$ for which the low k_a/k_d value of 0.74 was found in several experiments compared with 16 for

diethyl ether. In this case, it is clear that a cleavage reaction of the ether radical gives acetone, thereby depressing the value of k_a/k_d.

$$i\text{-Pr-}\overset{\cdot}{O}CMe_2 \longrightarrow i\text{-Pr}\cdot + Me_2CO \qquad (5)$$

In cases where the values of k_a/k_d were measured both at 100° and 50°, the increase in value found at the lower temperature is due to the greater decrease in the rate of cleavage that has the higher activation energy, estimated[11] at about 13-15 kcal/mol compared to about 5 kcal/mol for the abstraction process.

E. Comparison of Reactivity Towards t-BuO· and t-BuO$_2$· Radicals

The last two columns of Table V provide a comparison of the relative reactivity of several compounds towards t-BuO$_2$· and t-BuO radicals. (Since none of the values of k_p were corrected for initiation by hydroperoxide, the comparisons have probable error limits of about 20% in most cases.) Comparison of the relative k_p's for oxidation shows there is little difference between the oxygenated compounds at 50° on a per hydrogen basis, but all of them are about five times more reactive in oxidation than isobutane, which is included from earlier work for comparison.

The values of k_p for the alcohol and ketone at 100° are also very similar on a per hydrogen basis, but k_p for isobutane is about one-half to one-third as large. An earlier experiment with i-PrOAc shows that it is too unreactive for accurate comparison.

Cross-comparison of these values with k_a/k_d values for t-BuO· radical in the last column fails to show a good correlation between the two measures of reactivity. Thus k_a/k_d values for Et_2O and i-Pr_2CO at 50° are 4 and 1.5 (on a per hydrogen basis) for t-BuO· and 0.9 and 1.2 for t-BuO$_2$·. For Et_2O and i-BuH the ratios are 4 and 6.7 for t-BuO· and 0.9 and 0.23 for t-BuO$_2$·. At 100°, the values for Et_2O, i-PrOH and i-PrOAc are in reasonable agreement with k_p values however the isobutane values are out of line.

Although there are too few data on which to base any firm conclusions, the trend suggests that electronic or sterically similar compounds will have similar relative reactivities towards both radicals. For any given compound, we might expect factors of two to three in their reactivity towards either radical. Some other procedure is needed to evaluate relative reactivities in oxidation, since the hydroperoxide technique generally leads to complications with oxygenated molecules.

It is of interest that the two radicals have such similar relative reactivities despite the fact that reactivities differ. The absolute reactivity of t-BuO· radical is probably about 10^5 greater[11] than t-BuO_2· radical at 50^0 to 100^0. Clearly, reactivity and selectivity are not mutually exclusive properties; nor does low reactivity as in the case of peroxy radical imply high selectivity.

F. Comparison of Impact Sensitivity and Reactivity in Autoxidation

Section IIb discusses correlations between impact sensitivity and physical or chemical properties of several classes of compounds. We have also measured the relative rates of oxidation of three of the compounds tested, i-PrOH, i-PrOAc, and i-Pr_2O (Table I, cont. and Table II). The similar sensitivity of i-PrOH and i-PrOAc in impact tests and the higher sensitivity of i-Pr_2O are clearly different from the results in autoxidation measurements, where the alcohol and ether are many times more reactive than the ester. These results further substantiate the conclusion of Section II that physical properties, particularly flash points, are often more important than specific chemical reactivity.

This conclusion is further confirmed by the results with the hydrocarbon series--cyclohexane, hexane, dodecane and polyethylene where we would expect the relative reactivity in autoxidation to

be similar for all three n-alkanes and higher for cyclohexane. Again, this is clearly at variance with impact sensitivity measurements, the results of which are correlated well with flash points of the hydrocarbons.

G. Reaction of Trimethylaluminum with Oxygen and with Methanol

1. Background

A few classes of organic compounds are known to undergo spontaneous reaction with oxygen at or near room temperature. Trialkylboranes and trialkylaluminums are conspicuous examples and some of the lower members of these series are spontaneously flammable at 25°C. Thus, we decided to investigate, at least briefly, the mechanism of the oxidation of trimethylaluminum to learn how this class of compound differs from most other organic compounds in its very fast and vigorous reactions with oxygen.

Our objectives in this investigation were to establish the kinetics of oxidation; evaluate the rate constant and (if possible) the rate parameters, from which to deduce a possible mechanism; and to examine the initial oxidation products by low-temperature nmr.

Prior to starting experimental work, a literature search was made on the controlled oxidation of boron and aluminum alkyls. The ready oxidation of trialkylboranes has been recognized for about a hundred years. The first careful study of the controlled oxidation, however, was that of Johnson and Van Campen[15] using tri-n-butylborane near room temperature. They found that one mole of oxygen was consumed for each mole of tri-n-butylborane and the product was the di-n-butoxyboronate.

$$(n\text{-}Bu)_3B + O_2 \longrightarrow (n\text{-}BuO)_2B\text{-}Bu\text{-}n$$

They suggested that the first step was coordination between oxygen and the boron atom, followed by reaction with a second mole of trialkylborane to give the final product. However, later work has shown that the coordination product, $R_3\bar{B}O_2^+$, rapidly rearranges to the dialkyl alkylperoxyborane, which is the first stable product.

Oxidation of trimethylborane proceeds readily even at -196°C to give, quantitatively, the corresponding dimethyl methylperoxyborane (Me_2BOOMe).[16] At room temperature the dialkyl alkylperoxyborane is rapidly reduced to the dialkyl alkylboronate [$RB(OR)_2$] through further reaction with trialkylborane.[17] However, this reduction can be minimized by dilution. Dimethyl methylperoxyborane is the only product isolated from trimethylborane-oxygen mixtures at 25°C in the gas phase.[18] A mechanism that adequately accounts for these observations is:

$$R_3B + O_2 \rightleftarrows R_3\bar{B}O_2^+ \qquad (5)$$

$$R_3\bar{B}O_2^+ \rightarrow R_2BO_2R \qquad (6)$$

$$R_2BO_2R + R_3B \rightarrow 2R_2BOR \qquad (7)$$

Although Coffee and Davies[19] have offered some evidence favoring a free-radical mechanism for the oxidation of trialkylboroxines [$(RBO)_3$], the bulk of the evidence still favors the molecular oxidation process shown in equations 5-7.

Trialkylaluminums have been studied to a much lesser extent than have the boron compounds.[20-22] The available evidence suggests a mechanism similar to that for the boranes,[20] except that reduction of the peroxide is much faster and little peroxy intermediate is isolated from such oxidations even at -70°C.

Two recent studies of the gas phase oxidation of triethylaluminum[23] and trimethylaluminum[24] provide evidence that radicals are generated at

some stage of the oxidation. Ignition of trimethylaluminum is strongly influenced by additives such as amines or olefins. Apparently they enter into the chain reactions with species such as $Me_2AlO\cdot$.[24] However, in these studies reactions were not isothermal and radical formation may have arisen through thermal decomposition of the intermediate dimethyl methylperoxyaluminum.

2. Reaction With Oxygen

Several oxidation experiments were carried out with Me_6Al_2 and oxygen at -140°C in CF_2Cl_2 solvent in which the Me_6Al_2 was added by distillation from the vacuum line and the decrease in oxygen pressure (initially at 140 torr) was noted on a Wallace and Tiernan gage. The procedure gave erratic and unrealiable kinetic data because of the fast initial solubilization of oxygen in the solvent and because of the uncertainty in the amount of Me_6Al_2 added; vacuum transfer of Me_6Al_2 is slow and much of it deposits on the sides of the reaction vessel, well above the solvent line.

Some additional runs were carried out using the apparatus shown in Figure 12 using improved procedures for adding reactants and correcting for solubilization. Known amounts of Me_6Al_2 were injected into the nitrogen-filled reaction vessel at 25° from a microliter syringe. The port was sealed off and the vessel was evacuated and cooled to between -140° and -130°; a known amount of CF_2Cl_2 was condensed into it, and the mixture was stirred magnetically until thermal equilibrium was reached. A measured amount of oxygen was then added to the system from a gas-buret and allowed to dissolve and react for ~1000 seconds before changes in pressure were noted with time. A blank experiment without Me_6Al_2 showed that equilibrium solubility was achieved after ~1000 seconds.

Five runs were made between -140° and -130° on two solutions of Me_6Al_2 in $CFCl_2$; after oxidation had proceeded to completion or nearly so, additional oxygen was added at a new temperature. The data are summarized in Table II. Since amounts of oxygen and Me_6Al_2 were nearly

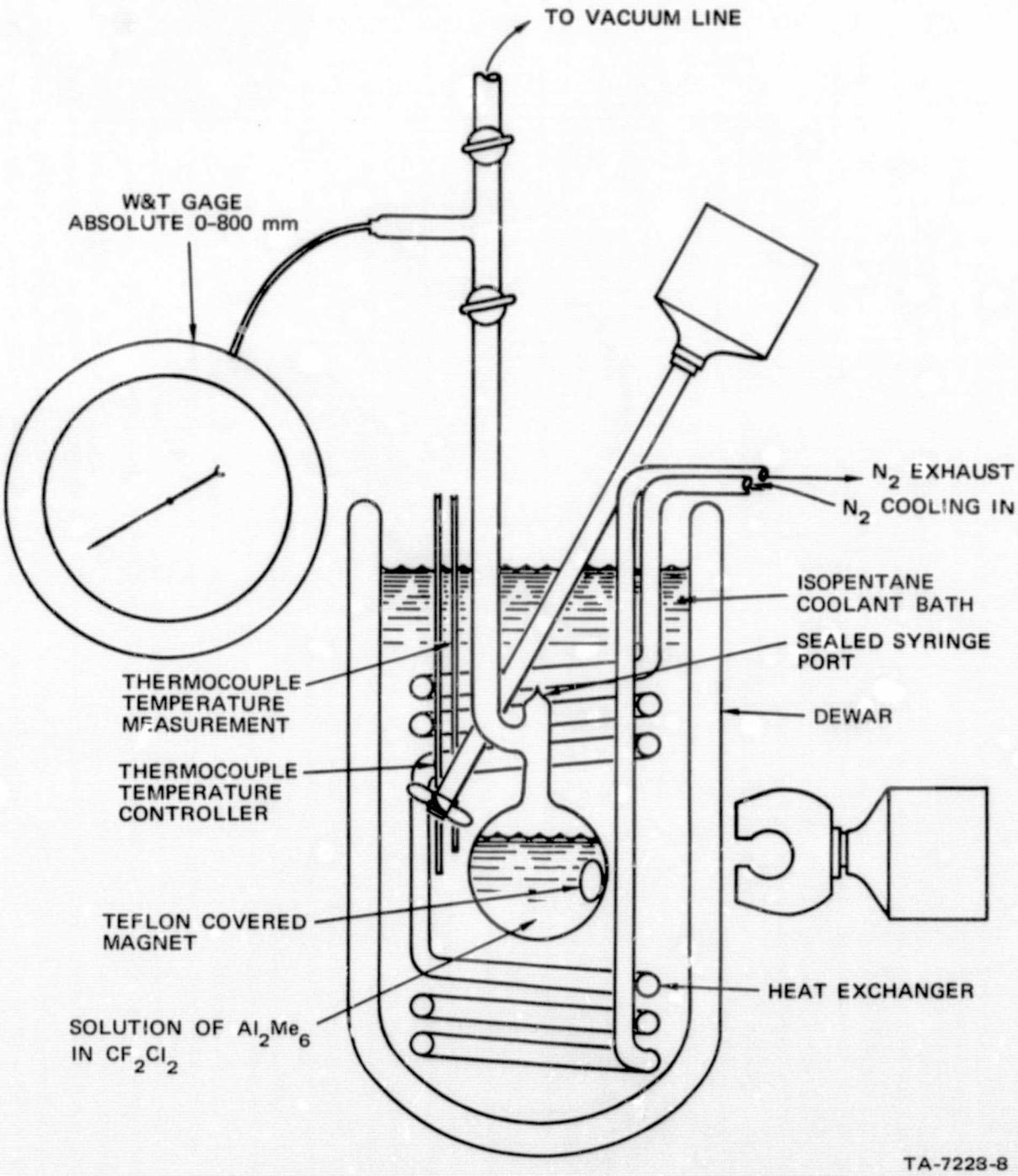


FIGURE 12 APPARATUS FOR LOW-TEMPERATURE OXIDATION OF Me_6Al_2

Table IX

REACTION OF OXYGEN WITH Me_6Al_2 IN CF_2Cl_2

Run	Temp. °C	$[Me_6Al_2]_o$ M, μmoles	$(O_2)_o$[a] μmoles	ΔO_2 μmoles	$k_2 \times 10^2$ l/mol sec
10a	-143	0.015, 629	284	225	1
10b	-133	--	1340	802	6.7[b]
11a	-142	0.021, 875	867	867	1.5
11c	-134	--	795	677	2.6[b]
11d	-133	--	794	0	--

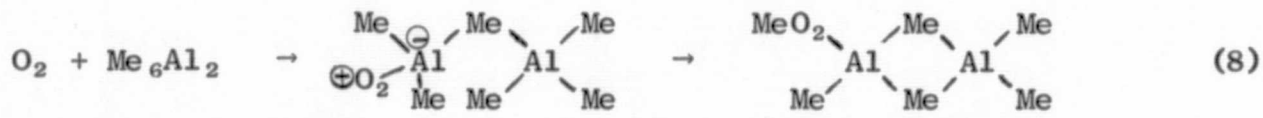
[a]Oxygen is at ~50 torr.
[b]These rate constants refer to oxidation of $MeO_2Me_5Al_2$.

equivalent, the data were plotted as second order in the form log $\frac{[Me_6Al_2]}{[O_2]}$ versus time. The concentration of oxygen as a function of pressure was estimated from blank experiments where oxygen pressures were noted on the presence and absence of a known volume of CF_2Cl_2 at -140°.

Kinetic runs 10b and 11a consisted of two points only and therefore are of doubtful validity. Although straight line relationships were observed for the other (3- to 6-point) runs, the temperature dependence (log k_2 versus $\frac{1}{T}$) showed appreciable scatter.

There are two major sources of error in these measurements. One is the rapid solubilization of oxygen in CF_2Cl_2 which precludes measurements during the initial portion of the reaction. The second is oxidation of $MeO_2Al_2Me_5$ which is significant during some period of reaction with the first equivalent of oxygen and is the dominant process in runs 10b, 11c, and 11d. For these reasons we consider the kinetic data as qualitative only.

A mechanism consistent with these kinetic requirements is one in which oxygen acts as a nucleophilic species, displacing on the dimer with activation energy of about 5-7 kcal/mole (the A factor is assumed to be 10^9/sec).



(8)

The rate of rearrangement of the initial complex to the peroxy intermediate is probably very fast, but since this step is unimolecular it is probably not rate controlling. This is a somewhat surprising conclusion since oxygen is not a particularly strong nucleophile but appears able to effect this displacement with great facility.

The rate of oxidation of Me_6Al_2 and its first oxidation product, $MeO_2Al_2Me_5$, are very similar although no more than two moles of oxygen were absorbed for each mole of Me_6Al_5. Probably $(MeO_2)_2Me_4Al_2$ forms a trimeric species in which cleavage of the strong Al-O bonds by oxygen is too unfavorable to permit additional oxidation at the low temperatures employed in these experiments.

Nmr spectra of the oxidation mixtures were taken at -60° before and after warming to 20° to convert the peroxy to the methoxy group. The spectra shown in Figure 13 show the presence of a multiplet at τ 5.97, which on warming disappears with concommitant growth of the MeO multiplet at τ6.49; Me-Al bands around τ10.8 also decreased in an amount corresponding to the growth of the τ6.47 band. Attempts were made to measure the rate of this rearrangement, but the results were erratic.

A trace of ethane is observed in the oxidation mixture as an nmr band at τ9.13. This must arise from coupling of two methyl radicals, the origins of which remain obscure. It is unlikely that any free radical chain reaction is associated with the low temperature oxidation although such processes may well be important at higher temperatures and undoubtedly play a role in the combustion of alkyl aluminums. It has been shown[25] that inhibitors do not affect the initial rate of oxidation of Me_6Al_2 at 25° although the same inhibitors do retard the oxidation of many other organometallic compounds.

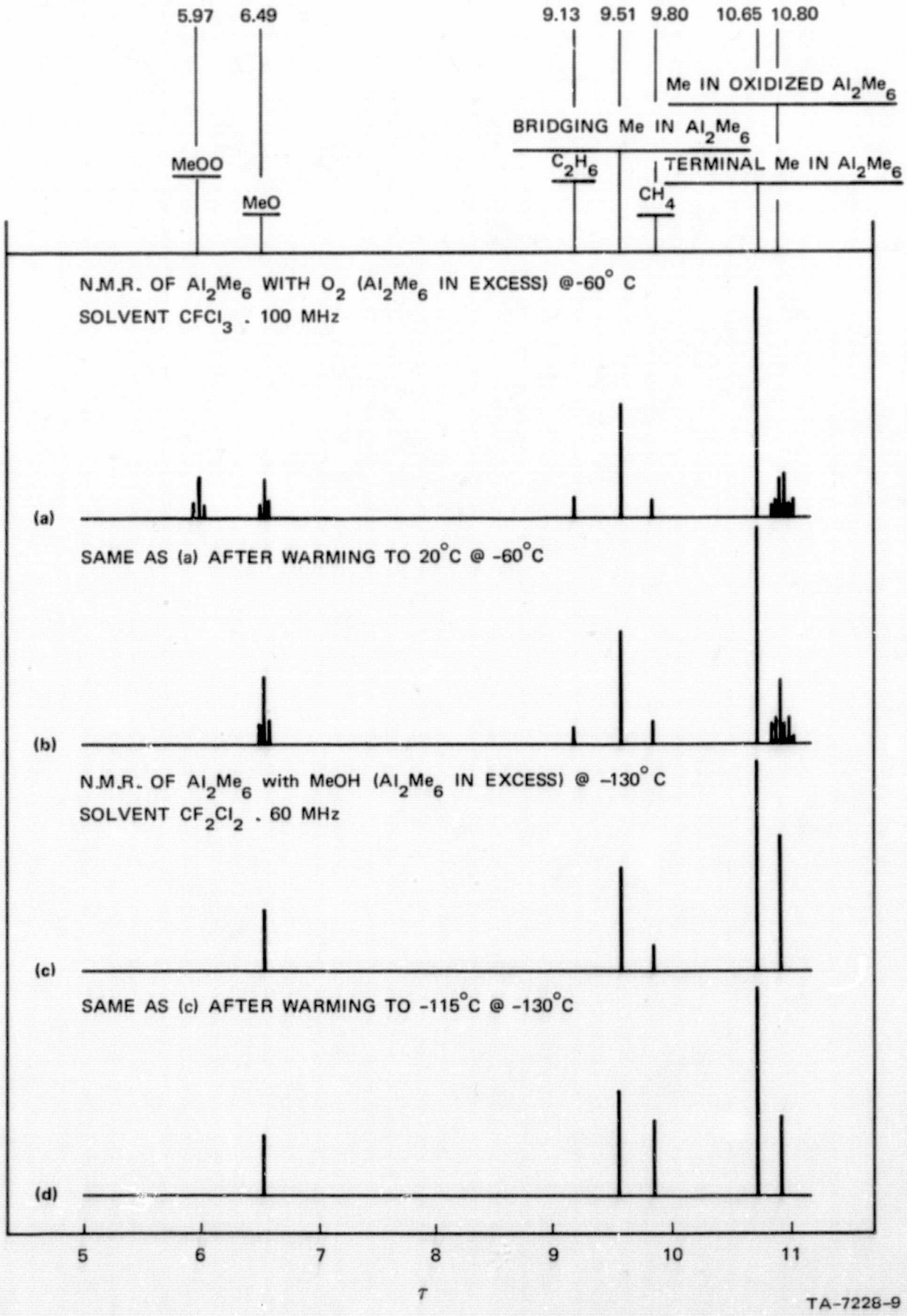
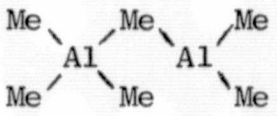


FIGURE 13 Nmr SPECTRA OF REACTIONS OF Me_6Al_2 WITH O_2 OR MeOH AT LOW TEMPERATURE

Rate constants measured in these and earlier experiments for the reaction of oxygen with Me_6Al_2 are all between 10^{-3} and 10^{-2} l/mol sec. We estimate[26] that the concentration of monomeric Me_6Al_2 is about 10^{-14} M in a solution 0.01 M in dimer at -140°C. Since the concentration of oxygen is also about 0.01 M, the observed rate cannot be caused by reaction of monomer, but must involve dimer and oxygen with a specific rate constant of about 10^{-2} l/mol/sec. We can also exclude a mechanism in which the oxygen adds to the half dimer,



(9)

on the basis that the estimated rate constant for methyl exchange through this half dimer is about 10^{-9} sec and ring opening must be rate controlling.

3. Reaction of Methanol with Me_6Al_2

Reactions of alcohols with Me_6Al_2 give alkoxy substituted aluminum methyls and methane. The reaction is of interest in connection with the oxidation of Me_6Al_2 because of the similarity of mechanisms and the expected identity of reaction products after warming the mixtures to 25°. Thus, spectra of such products would assist in identifying the principal bands in the products from oxidation.

A known amount (153 μmoles) of Me_6Al_2 contained in a tared syringe was added to 2 ml CF_2Cl_2 in a stirred round-bottomed flask attached to the vacuum line. The solution was then cooled in a constant temperature bath and about one equivalent of methanol was added from the toepler pump. Methane evolution was followed with time initially at -126° through use of the toepler pump. After a period equal to one or two half-lives, the reaction temperature was changed to -123° and another series of measurements was carried out. The procedure was repeated between -116° to -113°. Finally, the mixture was warmed to -23° to complete the reaction and to obtain a value for the total methane evolved. At each of the three temperatures, the log of $(CH_4)_\infty - (CH_4)_t$ was plotted versus time (first order). Straight line relationships were found, indicating that the rate controlling step in the addition of the first equivalent of methanol is formation of methane.

$$MeOH + Me_6Al_2 \xrightarrow{\text{fast}} MeO(H)Al_2Me_6 \xrightarrow{\text{slow}} MeOAl_2Me_5 + CH_4 \qquad (10)$$

Second and third equivalents of methanol were then added to the same mixtures at -116° and -70°. Fourth, fifth, and sixth equivalents of methanol were successively added at -23°, -10°, 0°, and 3°, and methane evolution versus time again measured at -23°. The data appeared to fit a second-order rate law, and the reaction of each additional molecule of methanol was slower than the previous one. From these results we conclude that addition of methanol to the tetramethoxydimethylaluminum is slow compared with formation of methane. These results are summarized in Table X.

$$MeOH + (MeO)_4Al_2Me_2 \xrightarrow{\text{slow}} (MeO(H))(MeO)_4Al_2Me_2 \xrightarrow{\text{fast}} (MeO)_5Al_2Me + CH_4 \qquad (11)$$

The kinetic parameters for first-order rate constants for evolution of methane were estimated from the temperature dependence for addition of the first equivalent of methanol at -126°, -123°, and -116° (Table X). A plot of 1/T versus log k_1 gave $k_1 = 10^{11.5\pm1}\ ^{-11\pm1}/\theta$. These parameters

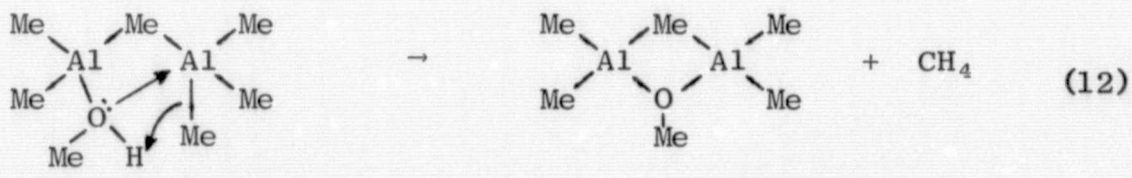
Table X

REACTION OF METHANOL WITH Me_6Al_2 IN CF_2Cl_2
(conc. in M)

Run	Temp. °C	$[MeOH]_o$	Reactant	$[Reactant]_o$	Evolved $[CH_4]$	k/sec x 10^6
6a	-133	0.100	Me_6Al_2	0.280	0.017	2.8
7b	-126	0.050	Me_6Al_2	0.068	0.009	10
7a	-123	0.077	Me_6Al_2	0.085	0.027	25
6c	-121	0.090	Me_6Al_2	0.090	0.085	52
7c	-116	0.041	Me_6Al_2	0.059	0.029	60
7d	-116	0.096	$Me_5Al_2(MeO)$	0.085	0.083	140
8d	-116	0.054	Me_6Al_2	0.030	0.055	105
9a[a]	-115	0.068	Me_6Al_2	0.100	0.068	280±100
6b	-113	0.090	Me_6Al_2	0.180	0.065	180
7e	-23	0.107	$Me_2Al_2(OMe)_4$	0.085	0.104	k_2(1/mol sec) = 2.6×10^{-3}

[a] Measured by nmr.

are reasonably consistent with a mechanism involving a four-membered transition state.



(12)

These data give no information concerning fast metathetical reactions that probably occur between $(MeO)_2Al_2Me_4$ and Me_6Al_2, to give $2MeOAl_2Me_5$ and to give trimers in which the Al-O bonds slow the addition of methanol in much the same way as occurs in oxidation.

A mixture of methanol and excess Me_6Al_2 in CF_2Cl_2 was prepared and examined by nmr at -130°, warmed to -115° for 5 min, recooled to -130° and reexamined. The spectra in Fig.13c and d show how the methane band at τ9.80 grows at the expense of the methyl group at τ10.80; no change was found in the methoxy band at τ6.49 even though it changed from

$$Me\overset{H}{\underset{+}{O}}\text{-}Al \text{ to } MeO\text{-}Al.$$

The close, though not identical, resemblance between nmr spectra from reaction of Me_6Al_2 with oxygen and with methanol shows that the products from the two reactions (after warming) are very similar, as expected. The complex multiplets around τ6.49 (MeO) and τ10.80 (Me-) from oxidation probably arise from a mixture of $MeOAl_2Me_5$ species having differing degrees of polymerization.

H. Oxidation of Trifluoromethyl Radical

We have previously shown that the photolysis of trifluoromethyl iodide in oxygen-saturated $CFCl_3$ at -100°C gave only a mixture of COF_2, SiF_4, and I_2.[1] No evidence for any bis-trifluoromethyl polyoxide or peroxide was detected by oxygen evolution, nmr, or ir. We concluded that iodine or iodine atoms somehow converted trifluoromethyl peroxy and/or trifluoromethoxy radicals directly to COF_2.

To test this conclusion and to verify our previous idea that oxidation of CF_3 radicals at low temperatures should produce the corresponding polyoxides, we examined the photolysis of hexafluoroazomethane[27] in oxygen-saturated $CFCl_3$ and pentane at -60 and -100°C, respectively. The reactions expected are:

$$CF_3N_2CF_3 \xrightarrow[-60 \text{ to } -100^\circ C]{h\nu} 2CF_3\cdot + N_2 \qquad (1)$$

$$CF_3\cdot + O_2 \longrightarrow CF_3O_2\cdot \qquad (2)$$

$$2CF_3O_2\cdot \rightleftharpoons CF_3O_4CF_3 \qquad (3)$$

$$CF_3O_4CF_3 \xrightarrow{> -40^\circ C} 2CF_3O\cdot + O_2 \qquad (4)$$

$$\xrightarrow{> -40^\circ C} CF_3O_2CF_3 + O_2 \qquad (5)$$

$$CF_3O_2\cdot + CF_3O\cdot \longrightarrow CF_3O_3CF_3 \qquad (6)$$

Reactions 1 to 3 should proceed readily even at -100°C. However, dissociation of the tetroxide (reactions 4 and 5) should be slow at temperatures below -40°C in contrast to the analogous reactions of di-t-butyl tetroxide[28] which decomposes above -70°C. Both the trioxide and peroxide[29] are thermally stable at 25°C.

Two photolysis experiments were carried out with $CF_3N_2CF_3$ and O_2, one in $CFCl_3$ at -60°C and one in pentane at -100°C. The experimental conditions and results are given in Table XL. Both experiments were carried out by irradiating the reaction mixtures in Pyrex with light from a medium pressure 200W point-source mercury lamp (PEK-201). After irradiation, the mixtures were degassed, nitrogen evolution was measured, and oxygen uptake was estimated by taking the difference between initial and final amounts of oxygen.

In experiment 1, the mixture was warmed to 0°C where any oxygen evolved from reactions 4 or 5 could be measured; none was found. In experiment 2, the irradiation was done at -100°C and oxygen evolution was measured at -60 and 25°C following the nmr analysis. Again no oxygen was found.

Both experiments gave SiF_4, COF_2, and $CF_3O_nCF_3$ (n = 2-4). Experiment 2 is notable in showing nmr bands for $CF_3O_4CF_3$, $CF_3O_3CF_3$, and $CF_3O_2CF_3$ at -70°C after warming the mixture briefly to 25°C to decompose some tetroxide. The presumption that the unstable species with a ϕ = 69.73 is indeed $CF_3O_4CF_3$ rests on the chemical shift similar[29] to those of trioxide and peroxide and to its ready decomposition to those products on warming. Unfortunately, no evolved oxygen, expected to a accompany reactions 4 and 5, was detected. Instead an equivalent amount of nitrogen was found by gas analysis. This could be experimental error and will be checked.

More than half of the CF_3 groups found in the products were as dimer, CF_3CF_3. This is probably the result of caged recombination of $CF_3\cdot$ from the azo compound and is analogous to our finding[28] of 80-90% cage recombination of t-butyl groups from azoisobutane under similar conditions.

Although material balances on CF_3 and ΔO_2 are poor, the experiments do confirm our assumptions regarding the probable mechanism of oxidation of $CF_3\cdot$ radical. Iodine or iodine atoms clearly interfere with the sequence of reactions 3-6, but no satisfactory explanation is available. Even in experiment 2 where iodine is completely absent a significant fraction of oxidized $CF_3\cdot$ forms CF_2O. Thus more than one pathway exists for the conversion:

$$CF_3O_2\cdot \rightarrow CF_2O$$

Table XI

PHOTOLYSIS OF $CF_3N_2CF_3$ IN OXYGEN-SATURATED SOLVENTS

Initial Conditions	Expt. 1	Expt. 2	
Solvent	$CFCl_3$	$n\text{-}C_5H_{12}$	
Temp., ^oC	-60	-100	
Time, hr	21	17.4	
$[CF_3N_2CF_3]_o$, μmoles M	0.35[a]	0.20[d]	
O_2, μmoles	569	294[e]	
PRODUCTS BY GAS ANALYSIS, μmoles			
Evolved N_2	119[b]	45[b]	
ΔO_2	166[b]	44	
Evolved O_2	0	0[f]	
PRODUCTS BY NMR, μmoles			
		-70°C	25° [g]
$CF_3O_4CF_3$	-	23	14
$CF_3O_3CF_3$	-	-	8
$CF_3O_2CF_3$	13	-	
COF_2	-	16	12
SiF_4	70[c]	5	3
CF_3CF_3	50	53	50
ΣCF_3	161	171	156

[a]Contained ~10% CF_3I. [b]Measured at reaction temperature. [c]Counted as 35 μmoles COF_2. [d]Purified by glc; no CF_3I impurity by nmr. [e]Circulated through solution at 60 mm pressure. [f]Measured at -70 and 25°C. [g]Measured at -70° after warming to 25° for a few minutes.

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